

PROCEEDINGS  
OF THE  
NATIONAL ACADEMY OF SCIENCES  
INDIA  
1959

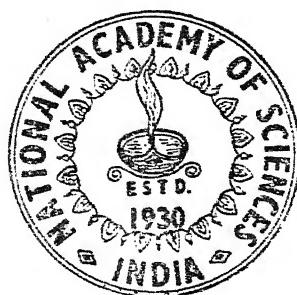
---

Vol. XXVIII

SECTION - A

Part VI

---



NATIONAL ACADEMY OF SCIENCES, INDIA  
ALLAHABAD

# THE NATIONAL ACADEMY OF SCIENCES, INDIA

(Registered under Act XXI of 1860)

Founded 1930

## Council for 1959

### President

Dr. M. S. Randhawa, M.Sc., D.Sc., F.N.I., F.N.A.Sc., I.G.S., New Delhi

### Vice-Presidents

Prof. P. L. Srivastava, M.A., D.Phil., F.N.I., F.N.A.Sc., Allahabad  
Prof. A. C. Joshi, D.Sc., F.N.I., F.N.A.Sc., Solan

### Honorary Treasurer

Prof. S. Ghosh, D.Sc., F.R.I.C., F.N.I., F.N.A.Sc., Allahabad

### Foreign Secretary

Dr. R. K. Saksena, D.Sc., F.N.I., F.N.A.Sc., Allahabad

### General Secretaries

Dr. R. N. Tandon, M.Sc., Ph.D., D.I.C., F.N.A.Sc., Allahabad  
Dr. K. N. Mathur, D.Sc., F.Inst.P., F.N.A.Sc., New Delhi

### Members

Prof. N. R. Dhar, D.Sc., F.R.I.C., F.N.I., F.N.A.Sc., Allahabad  
Dr. D. N. Wadia, M.A., D.Sc., F.R.S., F.G.S., F.A.S., F.N.I., F.N.A.Sc.,  
New Delhi  
Prof. S. Ranjan, M.Sc., D.Sc., F.N.I., F.N.A.Sc., Allahabad  
Prof. W. D. West, D.Sc., F.N.I., F.N.A.Sc., Sagar  
Prof. K. Banerji, D.Sc., F.N.I., F.N.A.Sc., Allahabad  
Prof. R. Misra, M.Sc., Ph.D., F.N.I., F.N.A.Sc., Varanasi  
Prof. M. D. L. Srivastava, D.Sc., F.N.A.Sc., Allahabad  
Prof. B. N. Prasad, Ph.D., D.Sc., F.N.I., F.N.A.Sc., Allahabad  
Prof. P. S. Gill, M.S., Ph.D., F.A.P.S., F.N.I., F.N.A.Sc., Aligarh

---

The *Proceedings of the National Academy of Sciences, India*, is published in two sections: Section A (Physical Sciences) and Section B (Biological Sciences). Six parts of each section are published annually.

The Editorial Board in its work of examining papers received for publication is assisted, in an honorary capacity, by a large number of distinguished scientists. Papers are accepted from members of the Academy *in good standing*. In case of a joint paper, one of the authors must be a member of the Academy. The Academy assumes no responsibility for the statements and opinions advanced by the authors. The papers must conform strictly to the rules for publication of papers in the *Proceedings*. A total of 50 reprints are supplied free of cost to the author or authors. The authors may have any reasonable number of additional reprints at cost price, provided they give prior intimation while returning the proof.

Communications regarding contributions for publication in the *Proceedings*, books for review, subscriptions etc., should be sent to the General Secretary, National Academy of Sciences, India, Lajpatrai Road, Allahabad-2 (India).

**Annual Subscription for each Section : Rs. 30 (Inland); 60 sh. (Foreign)**

**Single Copy : Rs. 5 (Inland); 10 sh. (Foreign).**

PROCEEDINGS  
OF THE  
**NATIONAL ACADEMY OF SCIENCES**  
**1959**

---

VOL. XXVIII

SECTION - A

PART VI

---

**CURVE OF GROWTH ANALYSIS OF  $\alpha$  PERSEI FROM  
NEUTRAL IRON LINES**

*By*

R. S. KUSHWAHA

*Department of Astrophysics, University of Delhi*

[Received on 12th December, 1959]

**ABSTRACT**

The curve of growth analysis of  $\alpha$  Per. has been carried out with the help of strong absorption lines of neutral iron only from high dispersion spectrograms taken at Victoria. The main feature of this study is to investigate whether or not for such a giant star the choice of Milne-Eddington model or Schuster-Schwarzschild model of atmosphere has any appreciable effect on the physical parameters of the atmosphere. Most of the  $f$ -values used are laboratory values. For some lines theoretical values were reduced to the laboratory scale. From the study it is found that the effect of the choice of the model of atmosphere lies well within the probable error. Thus it is immaterial which model we use for these super giant stars. From this analysis the following parameters are found.

Turbulence velocity    8.5 Km/sec.

Excitation temperature  $4800^\circ \pm 300^\circ$  K.

Number of atoms in the ground state of FeI, long  $N_a = 17.9$

**INTRODUCTION**

Such studies for  $\alpha$  per., were done before by Struve and Elvey (1934), Wright (1944) and Steel (1945). The present results are based on new equivalent width measurements of high dispersion plates taken at Victoria. The present study was carried out with the intention to investigate if the choice of Milne-Eddington model or Schuster-Schwarzschild model for the stellar atmosphere has any appreciable effect on the physical parameters of the atmosphere. Also in this study only the strong absorption lines of FeI, for most of which laboratory  $f$ -values are available, are used.

### OBSERVATIONAL MATERIAL

These high dispersion spectrograms used in the present study were taken at Dominion Astrophysical Observatory with 72-inch telescope. The total spectrum from  $\lambda$  3700 to  $\lambda$  6750 was covered in three parts. For the range  $\lambda$  3700 to  $\lambda$  4500 third order of Wood-grating was used in Littrow mounting. The second order of the same was used for  $\lambda$  5150 to  $\lambda$  6750. To cover the range  $\lambda$  4020 to  $\lambda$  5600 a three prism spectrograph was used. The original dispersions obtained in these spectrograms were  $4\cdot4\text{A}^\circ/\text{mm}$ ,  $7\cdot0\text{A}^\circ/\text{mm}$  and from  $4\cdot8$  to  $19\text{A}^\circ/\text{mm}$  respectively. The correction for the Rowland ghosts were applied in the usual manner.

Two or three plates of each region of the spectrum were run through the microphotometer. Then they were changed into intensity tracing by using the intensitometer designed by Beals (1944). Thus the tracings were magnified two hundred fold. These were superposed on one another to get the mean observed profiles of the absorption lines avoiding many inherent errors in photometry like plate grains, inaccurancies in drawing calibration curves and the position of the continuum. The identifications were made with the help of Miss Moores' Revised Multiplet Tables (1945). The areas of the mean line profiles were measured with the help of planimeter for about hundred and thirty lines of natural iron. For the lines in the wings Thackeray's (1936) simple relation was used. These final measurements are listed in the following table.

*Table of equivalent widths of FeI absorption lines in the spectrum of a Per.*

Wave length	Lower Ext. Pot.	$8 + \log f g\lambda$	$6 + \log \frac{W}{\lambda}$	Weight
3709.257	0.911	6.423	2.116	1
3719.949	0.000	6.296	2.140	2
3733.332	0.110	5.536	2.103	2
3737.143	0.051	6.224	2.308	1
3758.247	0.954	7.022	2.039	2
3763.805	0.986	6.831	2.155	2
3767.206	1.007	6.687	2.140	1
3787.893	1.007	6.286	1.991	2
3790.095	0.986	5.552	1.977	1
3795.014	0.986	6.350	2.209	1
3798.523	0.911	5.997	2.218	1
3799.560	0.954	6.282	2.231	1
3812.964	0.954	6.098	1.972	2
3815.853	1.478	7.252	2.108	2
3820.438	0.855	7.071	2.106	3
3824.454	0.000	5.544	2.242	2

Wave length	Lower Ext. Pot.	$8 + \log f g\lambda$	$6 + \log \frac{W}{\lambda}$	Weight
3825·893	0·911	6·935	2·102	2
3827·834	1·551	7·218	2·186	1
3834·235	0·954	6·804	2·324	1
3840·449	0·986	6·524	2·113	1
3841·060	1·601	7·140	2·094	1
3849·979	1·007	6·357	2·096	2
3856·383	0·051	5·656	2·046	1
3859·924	0·000	6·078	2·064	2
3865·535	1·007	6·249	1·923	2
3872·512	0·986	6·251	2·106	1
3878·029	0·954	6·212	2·084	1
3887·061	0·911	6·021	2·034	1
3895·669	0·110	5·302	2·054	2
3917·186	0·986	5·216	1·745	2
3920·271	0·121	5·356	1·955	2
3922·925	0·051	5·421	2·008	3
3927·935	0·110	5·449	2·194	2
4005·256	1·551	6·665	2·174	2
4063·597	1·551	7·267	2·116	3
4071·740	1·601	7·215	2·019	3
4132·060	1·601	6·657	2·089	2
4143·871	1·551	6·757	2·077	2
4191·436	2·458	8·301	1·929	2
4202·031	1·478	6·573	2·093	2
4206·702	0·05	3·411	1·522	2
4216·186	0·000	3·916	1·719	2
4222·219	2·439	7·942	1·768	3
4235·942	2·41	7·292	1·934	2
4250·125	2·46	7·132	1·784	2
4260·479	2·39	7·539	1·986	2
4271·159	2·44	7·252	1·791	2

Wave length	Lower Ext. Pot.	$8 + \log f g\lambda$	$6 + \log \frac{W}{\lambda}$	Weight
4282·406	2·17	6·990	1·827	2
4291·466	0·05	3·323	1·342	2
4325·765	1·601	7·238	2·028	2
4337·049	1·551	5·711	1·971	2
4375·932	0·000	4·303	1·741	2
4383·547	1·478	7·435	1·996	3
4389·244	0·051	3·060	0·973	2
4404·752	1·551	7·136	1·955	3
4415·137	1·601	6·666	1·976	2
4427·312	0·051	4·280	1·828	3
4430·618	2·21	4·992	1·628	2
4442·343	2·19	6·457	1·757	2
4447·722	2·21	6·499	1·682	2
4494·568	2·19	6·746	1·855	2
4528·619	2·17	6·978	1·886	2
4602·944	1·478	5·530	1·699	3
4871·327	2·853	8·477	1·880	2
4872·146	2·870	8·301	1·747	2
4890·765	2·863	8·477	1·809	2
4891·504	2·839	8·740	1·846	2
4896·449	3·867	7·891	0·892	3
4903·325	2·870	8·000	1·613	3
4919·000	2·853	8·544	1·837	2
4920·516	2·820	8·945	1·988	3
4938·822	2·863	7·903	1·620	1
4939·695	0·855	4·058	1·560	2
4973·106	3·943	8·352	1·207	2
4994·139	0·911	4·324	1·537	2
5001·872	3·865	8·954	1·784	2
5014·951	3·926	8·794	1·567	2
5022·243	3·967	8·623	1·536	2

Wave length	Lower Ext. Pot.	$8 + \log f g\lambda$	$6 + \log \frac{W}{\lambda}$	Weight
5044·220	2·839	7·301	1·186	1
5083·347	0·954	4·408	1·536	2
5150·843	0·986	4·262	1·477	2
5171·599	1·478	5·625	1·673	2
5192·350	2·985	8·419	1·765	2
5215·185	3·252	8·243	1·546	2
5216·278	1·601	5·448	1·663	2
5229·857	3·27	8·000	1·479	3
5232·946	2·927	8·819	1·830	3
5253·479	3·269	7·398	1·069	2
5263·314	3·252	8·097	1·497	2
5266·562	2·985	8·528	1·775	2
5269·541	0·855	5·948	1·929	2
5281·796	3·025	8·078	1·537	3
5307·365	1·601	4·628	1·379	3
5324·185	3·20	8·875	1·692	3
5332·903	1·551	4·764	1·336	3
5339·935	3·252	8·301	1·590	2
5341·026	1·60	5·630	1·670	3
5371·493	0·954	5·637	1·839	2
5393·174	3·227	8·176	1·598	3
5397·131	0·911	5·320	1·850	3
5405·778	0·986	5·461	1·811	3
5429·699	0·954	5·441	1·821	2
5434·527	1·007	5·244	1·754	3
5446·920	0·986	5·397	1·879	3
5455·613	1·007	5·272	1·886	2
5497·519	1·007	4·567	1·665	3
5506·782	0·986	4·601	1·617	3
5569·625	3·402	8·447	1·553	3
5572·849	3·382	8·681	1·645	2

Wave length	Lower Ext. Pot.	$S + \log f g\lambda$	$S + \log \frac{W}{\lambda}$	Weight
5576·097	3·415	8·146	1·397	3
5586·763	3·354	8·875	1·717	2
5615·652	3·318	9·041	1·724	2
5618·646	4·191	7·875	0·741	2
5624·549	3·402	8·301	1·506	2
5717·845	4·266	8·000	0·908	2
5753·136	4·242	8·352	1·151	2
5762·992	4·191	8·623	1·351	2
6232·655	3·638	7·653	1·013	2
6246·333	3·587	8·146	1·321	2
6336·837	3·671	8·130	1·203	3
6400·018	3·587	8·732	1·524	3
6408·033	3·671	8·020	1·135	2
6411·665	3·638	8·447	1·381	3
6639·726	4·587	7·653	0·268	1
6733·162	4·618	7·778	0·439	2
6752·725	4·618	8·130	0·232	2

#### *f*-VALUES

*gf* values for neutral iron lines were measured in the laboratory by King and King (1938). For some of the observed absorption lines specially for high potential ones these values could not be available from the laboratory measurements. For these lines theoretical values of  $\log S \frac{s}{\sum s}$  were used. To make these theoretical values consistent with the laboratory values these were also calculated for some other lines. From the comparison of the two it was found that they differed approximately by a constant value. From this comparison it was possible to reduce the theoretical values to the laboratory values. Thus a consistent set of *gf* values was used in this study.

#### CURVE OF GROWTH

The curve of growth is a graphical representation of the relation of the intensity of a absorption line and the number of active atoms *N* which produce it. From the theory it is found (Menzel 1936) that this relation can be plotted as  $\log \frac{W}{\lambda}$  against  $\log X_0$  which is given by the following equation.

$$\log X_0 = \log g i f \lambda - \frac{5040}{T} \chi_1 + \log \frac{N_a}{b(T)} \cdot \frac{\pi e^2}{m c} \cdot \frac{1}{\sqrt{\pi v}} \quad \dots \dots \dots \quad (1)$$

Where  $W$  is equivalent width of the absorption line,  $\lambda$ , the wave length,  $X_0$ , the optical depth at the centre of the line,  $g_1$ , the statistical weight,  $f$ , the oscillator strength  $T$ , the excitation temperature  $x_1$ , the excitation potential of the lower level of the atomic transition and  $N_a$  is the number of atoms in that stage of ionization. The other symbols have their usual meaning.

Theoretical curve of growth for Milne-Eddington model of atmosphere have been derived by Wrubel (1949). These curves are the plots of  $\log\left(\frac{W}{\lambda} \cdot \frac{c}{v}\right)$  against  $\log \eta_0$  for different values of damping constant  $\log a$ . Here  $v$  is the vector sum of turbulence velocity and thermal velocity.  $\eta_0 = \frac{\sigma v_0}{k v_0}$  the ratio of the fictitious scattering coefficient at the centre of the line to the continuous absorption coefficient at the centre of the line is given by :

where all these symbols have their usual meaning and

To decide which of these curves should be used one has to depend upon the lines in the damping part of the curve of growth. Fe I lines in the present spectrum are not sufficient to give any definite value of this constant. It appears that perhaps for these lines  $\log a = -3$  can give a sufficiently good representation. This gives the value of  $\Gamma/v$  of the order of  $10^{-7}$ .

To decide about the values of  $B^{(0)}/B^{(1)}$  one has to calculate these for the whole range of  $v$ . It is found to vary appreciably. Interpolation is carried out with the help of Wrubel's Table 3 (1949) to reduce all the readings to a single value of  $B^{(0)}/B^{(1)}$  in order to use the curve for the whole range of the spectrum. In the present case the curve for  $B^{(0)}/B^{(1)} = \frac{2}{3}$  was used for the whole range.

The observed curves of growth were plotted as  $\log \frac{W}{\lambda}$  against  $\log f.g_1\lambda$  for a set of mean excitation potentials each having a range of about  $\pm 0.05$  electron volt. Then these observational curves were fitted on to the theoretical curves as far as possible.

## TURBULENCE VELOCITY

The fit of the observed curve of growth on to the theoretical one is a matter of considerable personal judgment. When the best possible fit was obtained the difference in the ordinate  $\left[ \log \frac{W}{\lambda} \cdot \frac{c}{v} - \log \frac{W}{\lambda} \right]$  which gives the velocity  $v$ , was read for each of the observed curves. The scatter in this reading for the present case was found to be very small. Struve and Elvery (1934) have pointed out that for giant

and super giant stars the velocities determined from the curve of growth consist of the two velocities, turbulence velocity produced by the motions of the currents in the atmosphere on a large scale and the thermal velocities. Finally, therefore, the turbulence velocity was calculated from the equation

$$v^2 = v_0^2 + v_T^2$$

Where  $v_T$  is turbulence velocity and

In the last equation  $T$  is the temperature,  $\mu$ , the mean molecular weight for the stellar material,  $H$ , the atomic weight unit and  $k$ , the Boltzmann constant. Ultimately this gives the turbulence velocity of 8.5 Kilometers per second, which agrees very well with the results obtained by previous investigators.

## EXCITATION TEMPERATURE

From the fitting of the observed curves on the theoretical curve one gets the value of  $\log \eta_0 - \log f_{g1}\lambda$  for each mean excitation potential. From the equation (I) it is clear that when the reading of this horizontal shift is plotted against the excitation potential one would get a straight line

The slope of the this line gives the value of  $\frac{5040}{T}$  which gives the required excitation temperature. The actual temperature can be obtained from the least square solution. From the present analysis a temperature of  $4800^\circ \pm 300^\circ$  K is found as the excitation temperature for this star which also agree well with other published results.

### NUMBER OF ATOMS

From equation (2) one gets

$$\log \eta_0 = \log \frac{N_a \sqrt{\pi} e^2}{b(T) m c} - \log v + \log g_2 f \lambda = \frac{5040}{T} \chi_1 - \log K_v \quad \dots \dots \dots (6)$$

The value of  $K_V$  for this equation was derived from Chandrasekhar's tables (1946) using the relation  $\bar{K} = 1.42 \bar{K}(H)$ . Thus from the value of the constant term  $L$  in the equation (5) obtained from the least square solution one gets the value of  $\log N_a$ , giving the number of atoms in the ground state of FeI. Once more we see that the value,  $\log N_a = 17.91$ , obtained from the present work agrees well with the value ( $\log N_a = 17.74$ ) derived by Wright (1948).

## COMPARISON WITH SCHUSTER-SCHWARZSCHILD MODEL

Wrubel (1954) has also derived the theoretical curves of growth for Schuster-Schwarzschild model. These curves are calculated for different values of limb darkening. For the stars the limb darkening is quite uncertain quantity. Fortunately these curves do not differ very much specially in the region of the curve of growth which has to be used for the present work. Therefore any suitable guess

should be good enough for our purpose. Hence the value adopted was  $I^o/I' = 0.6$ . Where

is the law of limb darkening of the photosphere. The theoretical curve for this value of the ratio  $I^o/I'$  was interpolated between his curves by the formulae

and

where  $\left(\frac{W}{b}\right)_1$  and D are taken from Wrubel's Table 2 (1954).

To compare the results with those from Milne-Eddington model the same value ( $\log \alpha = -3$ ) for the damping constant was used again. The above analysis for the absorption lines of FeI was repeated in the same way. This analysis gave the following result. The turbulence velocity as 7.5 kilometers per second, the excitation temperature as  $4500^\circ \pm 300^\circ\text{K}$  and the number of atoms as  $\log N_\alpha = 17.97$ .

From these values it is quite obvious that the difference between these values and the corresponding values from the Milne-Eddington model are well within the probable errors. Thus it appears that for such stars like  $\alpha$  Persei the two extreme models of the atmosphere yield very similar results. As the real situation of the atmosphere is between the two extremes, it can very safely be concluded that these results do correspond to the real situation in the atmosphere of this star.

## TURBULENCE VELOCITY FROM IONIZED ATOMS

Wright (1948) has pointed out that the turbulence velocity for ionized atoms is quite different from that for the natural atoms.

To look into this question some lines of Fe II and Ti II were also measured. Unfortunately for these enough experimental  $f$  values are not available from the laboratory. A comparison of some whatever available from laboratory experiments with the theoretical values did not give any reasonable correlation. Hence the difficulty was realized in doing exactly what is needed. The only alternative left was to use the solar  $f$  values. Wright (1944) has derived a curve of growth for the sun with the aid of equivalent widths measured by Allen (1934 and 1938) and by himself from the Utrecht photometric Atlas of the solar spectrum (Minnart, Mulders and Hontgest 1940) combined with laboratory  $gf$  values for Fe I and Ti I lines measured in absorption by King and King. For a given line (solar value of  $\log \frac{W}{b}$ ) the corresponding  $\log X_{\odot}$  is read from this solar curve.

The observational curve of growth is plotted as  $\log \frac{W}{\lambda}$  against this solar  $\log X_{\odot}$ .

We have the equation for the star

and for the sun

subtracting we get

$$\log X_* - \log X_{\odot} = \log \frac{N_*}{N_{\odot}} \cdot \frac{b(T_{\odot})}{b(T_*)} - \log \left( \frac{v_*}{v_{\odot}} \right) - 5040 x_i \left( \frac{1}{T_*} - \frac{1}{T_{\odot}} \right) \dots \dots (12)$$

Again we fitted the observed curve to the theoretical curve as before. This time it was found that some of the lines did fall on the damping portion of the curve of growth. It appeared that if the damping constant lower than the Wrubel's lowest value is used than the observed curves for Fe I, Fe II and Ti II all can be fitted on to the same curve of growth without giving any differences in the turbulence velocities for the neutral atoms and the ionized atoms. Consequently the theoretical curve of growth for  $\log a = -3.4$  was extrapolated and finally adopted. This did not change the results for Fe I atom by any appreciable amount. We again plotted  $\log X_* - \log X_{\odot}$  against  $x_i$  for Fe II and Ti II. This gave a line whose slope was almost zero giving as a result the information that the excitation temperature of  $\alpha$  - persie is not very different from that of the sun which confirms the result obtained from Fe I lines.

It may be noted here that the lower value of damping constant actually corresponds to a value even lower than the classical value which does not seem to be very happy situation. If we avoid this lowering of the damping constant we find that the observational curves of growth for ionized elements are fitted best only when we have turbulence velocity for these different from those for neutral Fe I. Thus we confirmed the result due to Wright (1946) as also pointed out by Aller (1942) who also suggested that if this is right inter locking or emission arising from chromospheric effects might explain the discrepancy.

#### REFERENCES

1. Allen, C. W., 1934, *Mem. Comm. Solar Obs., Canberra*.
2. Allen, C. W., 1938, *Ibid*, No. 6.
3. Aller, L. H., 1942, *Ap. J.*, **95**, 73.
4. Beals, G. S., 1944, *Jour. Roy. Astr. Soc. Canada*, **38**, 65.
5. Chandrasekhar, S., 1946, *Ap. J.*, **104**, 450.
6. King, A. S. and King, R. B., 1938, *Ibid.*, **87**, 24.
7. Menzel, D.H., 1936, *Ibid*, **84**, 462.
8. Minnaert, Mulders, Houstgest, 1940. Amsterdam.
9. Moore, G. E., 1945, Revised Edition of multiplet Table of Astrophysical Interests Princeton Obs. Contr., 20.
10. Steel, H. R., 1945, *Ap. J.*, **102**, 43.
11. Struve, O. and Elvey, G. T., 1934, *Ibid*, **79**, 409.
12. Thackeray, A. D., 1936, *Ibid*, **84**, 433.
13. Wright, K. O., 1944, *Pub. Am. Astr. Soc.*, **10**, 338.
14. Wright, K. O., 1944, *Ap. J.*, **99**, 249.
15. Wright, K. W., 1946, *Jour. Roy. Astr. Soc. Canada*, Vol. XL 183.
16. Wright, K. O., 1948, *Pub. Dom. Astr. Obs., Victoria*, Vol. VIII, No I.
17. Wrubel, M. H., 1949, *Ap. J.*, **109**, 66.
18. Wrubel, M. H., 1954, *Ibid*, **199**, 51.

# CHEMICAL EXAMINATION OF THE LEAVES OF THE PLANT

## *TINOSPORA CRISPA*

### STUDIES ON MINERAL, BASIC AND NON-BASIC CONSTITUENTS

By

A. SINHA

*Pharmacological Laboratories, Division of Chemistry, Medical College, Agra*

[Received on 30th December, 1959]

The leaves of *Tinospora Crisp*, on complete incineration left a greyish white ash (yield 2·78%) of which 36·2% was water soluble. By the application of flame photometric and colorimetric techniques, the amounts of Na, K, Mg, Ca, Fe, Al, Cu and Zn have been found to be 328·39, 1285·80, 212·48, 256·16, 30·92, 20·64, 1·48 and 0·94 mg. per 100 g. respectively on dry weight basis.

From the basic constituent, two alkaloidal principles have been isolated and their derivatives prepared. The non-basic constituent contained three neutral bodies of which one, m. p. 95° - 97° has been characterised as a hydroxy compound,  $C_{12}H_{18}O_3$  and two sterols. One of these melt at 138° - 39° and has been identified as *r*-sitosterol. It also contained an essential oil and a mixture of fatty acids.

Under the research programme on systematic examination of Indian medicinal plants belonging to N. O. *Menispermaceas*, it was thought desirable to investigate *Tinospora crispa*, a climbing plant commonly known as *Vasanel* found in tropical and sub-tropical India and noted for its medicinal properties.<sup>1,2,3</sup> Preliminary examination of the leaves of the plant revealed the presence of an essential oil, colouring matters, mucilage, alkaloids, sterols and a mixture of fatty acids. Although, investigations have been carried out on the plant *Tinospora cordifolia* belonging to the same family by several workers in the past,<sup>4,5,6,7</sup> a survey of available literature reveals that no systematic chemical examination has been undertaken on any part of the plant *Tinospora crispa*. In view of the medicinal use of this plant, a systematic and detailed chemical examination of the leaves has been undertaken and the present communication is concerned with the investigations on the mineral, basic and non-basic constituents of the leaves.

#### EXPERIMENTAL

Leaves of *Tinospora crispa* were obtained from the local area for investigation.

#### EXAMINATION OF MINERAL CONSTITUENT

10 g. of the dried powdered leaves were incinerated in a muffle furnace at 500° for 2 hours when a greyish white ash (yield 2·78%) was obtained. Of this, 36·2% was water soluble and the water insoluble portion was soluble in dil. HCl. The ash on analysis was found to contain Na, K, Ca, Mg, Fe, Al, Cu and Zn as the basic radicals and Cl, SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, CO<sub>3</sub><sup>2-</sup>, and SiO<sub>3</sub><sup>2-</sup> as the acid radicals. For quantitative estimation, the method of Sylvester and Hughes<sup>8</sup> was employed. The estimation of Na, K, Mg and Ca has also been directly carried out from an aqueous extract of the leaves prepared by boiling 10 g. of the leaves in 150 c. c. of distilled water for an hour. The product was macerated mechanically in a blending machine for an hour after which it was again boiled for 30 minutes, cooled, diluted with water to 200 c. c. and filtered through Whatman filter paper No. 44. The filtrate was employed after proper dilution for the estimation of Na, K, Mg and Ca and

the readings were noted on an Eel Flame Photometer using respective filters for Na, K, Mg and Ca. Standard solutions of Na as NaCl, K as KCl, Mg as MgCl<sub>2</sub> and Ca as CaCl<sub>2</sub>, were used for comparison.

The estimation of Fe has been done in the ash by the method of Winter<sup>9</sup> by measuring the colour intensity of its thiocyanate, while that of Al by the method of Kolthoff<sup>10</sup> using hydroxy methyl anthraquinone. The quantitative estimation of Cu has been done by the method of Hanak<sup>11</sup> using potassium ferrocyanide for the development of colour. Zn has been estimated in the ash by Holland and Ritchie<sup>12</sup> method. The colorimetric measurements were made on a Klett Summerson Photoelectric Colorimeter, using filters of suitable transmission ranges. The quantities of Na, K, Mg, Ca, Fe, Al, Cu and Zn have been found to be 328·39, 1285·80, 212·48, 256·16, 30·92, 20·64, 1·48 and 0·94 mg. per 100 g. respectively on dry weight basis.

The leaves of *Tinospora crispa* contain low sodium and high potassium content (approx. ratio 1 : 4) and may be useful in certain diseases, e.g. hypertension, where the intake of potassium is desired to be higher with a corresponding lower intake of sodium. The leaves contain 0·94 mg. per 100 g. Zn which forms the prosthetic group of enzyme carbonic anhydrase that plays an important role in the transport of carbon dioxide by blood and its activity is directly or indirectly linked with the reactions in the acid-base equilibrium of the body.<sup>13</sup>

#### EXAMINATION OF BASIC AND NON-BASIC CONSTITUENTS

Preliminary successive extractions of the leaves with petroleum ether (b.p. 40°-60°), ether, benzene, chloroform and absolute alcohol yielded 0·90, 0·78, 0·45, 0·40 and 2·40% extractives respectively. The extracts from the first three solvents consisted of a sweet smelling, pale yellow essential oil and the latter two solvents yielded a greenish sticky residue. The water and alcoholic extracts of the leaves gave positive tests for reducing sugars, tannins and alkaloids while the petroleum ether and ether extracts responded to the tests for sterol.

#### EXAMINATION OF ACID EXTRACT

4·0 Kg. of the green leaves of *Tinospora crispa* were extracted with 1·5% H<sub>2</sub>SO<sub>4</sub> containing 0·4% sodium metabisulphite by percolation and with alcohol in a soxhlet extractor. The extract was collected and evaporated to dryness. The residue was dissolved in 200 c. c. of water and the total alkaloids present were precipitated with an excess of Dragendorff's reagent. The orange red precipitate (yield 12 g.) was washed with dil. HCl and then with water, dried and reextracted with alcohol in a soxhlet. For further purification, the alcoholic extract was decomposed with silver carbonate, re-extracted with alcohol, evaporated to dryness under reduced pressure and the residue (A) examined.

*Examination of alcohol soluble substance (A)* : The residue was dissolved in absolute alcohol and reprecipitated twice by diluting with an excess of benzene. It was filtered and the benzene insoluble substance was labelled as B. The filtrate, alcohol benzene liquor, on evaporation to dryness left a residue which was again extracted with benzene, the extract evaporated to dryness and the residue labelled as C. Fraction C on further purification, yielded a non-nitrogenous pale yellow crystalline solid which on repeated crystallisation from ether turned into fine needles, m. p. 112°. The quantity of this substance was not sufficient for further work.

*Examination of benzene insoluble substance (B) :* The substance was successively extracted with chloroform and water, the extracts were separately evaporated to dryness under reduced pressure when brown residues labelled as  $B_1$  and  $B_2$  respectively were obtained.

*Examination of chloroform soluble fraction  $B_1$  :* The brown coloured residue was dissolved in alcohol and precipitated with an excess of ether. The supernatant liquid did not contain alkaloid and was rejected. The precipitate was dried and re-extracted with chloroform. The extract on evaporation of the solvent left a pale yellow amorphous substance, m. p. 96°. This substance tasted intense bitter and was soluble in NaOH and alcohol but insoluble in ether and benzene. Found; C, 73.30; H, 7.42; N, 3.15%. The alkaloid yielded an orange red precipitate with Dragendorff's reagent, m. p. 223° (decomp.), an yellow picrate which resinified on drying and a dark brown precipitate with chloroplatinic acid not melting upto 300°.

*Examination of water soluble fraction  $B_2$  :* The brown residue was dissolved in alcohol and reprecipitated with petroleum ether. The supernatant liquid did not contain an alkaloid and was rejected. The brown precipitate was dissolved in absolute alcohol and resolved into two fractions chromatographically on Brockmann alumina column using alcohol and ethyl acetate-water (1: 15) as eluents. These fractions, however could not be rendered into solid or crystalline form. The alcohol fraction gave orange red precipitate with Dragendorff's reagent, m. p. 203° - 202°, a brown precipitate with 5% platinichloride which darkened at 186° but did not melt upto 300°, a brown picric acid derivative, m. p. 153° - 60° and a brown precipitate with 5% auric chloride, m. p. 104° - 105°.

The ethyl acetate-water fraction also yielded an orange red precipitate with Dragendorff's reagent, m. p. 112° - 14°, a brown precipitate with 5% platinichloride which resinified on drying, an yellowish brown picric acid derivative, m. p. 128° and a brown precipitate with 5% auric chloride, m. p. 171° - 172°.

With both the fractions, the hydrochlorides and oxalates were not obtained by treatments with HCl and oxalic acid whereas resinified products were obtained with picrolonic acid. The two fractions were found to have lowering action on blood pressure and depression of the heart (myocardium).

#### EXAMINATION OF ALCOHOLIC EXTRACT

The alcoholic extract of the leaves obtained in 2.4% yield after evaporation of alcohol was dark green in colour. It was successively extracted with petroleum ether (b. p. 40° - 60°), benzene, chloroform and water. No substance of any definite character could be isolated from the successive benzene, chloroform and water extracts. The extract from petroleum ether contained sterol and was labelled as Fraction D. The petroleum ether extract, Fraction D, on cooling to 0° deposited a light green substance labelled as Fraction  $D_1$  which on repeated crystallisation turned into white granules, m. p. 95° - 97°. This substance was soluble in petroleum ether, ether, benzene, chloroform and alcohol. The alcoholic solution of this substance set into a jelly like mass on cooling. Found: C, 69.36 ; H, 8.58% ; M. W. 223. (Calc. for  $C_{12}H_{18}O_3$  : C, 68.57 ; H, 8.57% ; M. W. 210). Its acetyl derivative prepared in the usual manner melted at 81° - 82°. The substance was found to be a hydroxy compound.

The petroleum ether extract (D) after removing the light green substance ( $D_1$ ) was evaporated to dryness and a residue ( $D_2$ ) was obtained. The residue  $D_2$  was

was dissolved in hot acetone and filtered. The acetone soluble and insoluble portions were labelled as D<sub>3</sub> and D<sub>4</sub> respectively. The filtrate was evaporated to dryness when a green waxy material (D<sub>5</sub>) was obtained. It turned into a white waxy mass on saponification and extraction with benzene. This substance was resolved into two fractions D<sub>5</sub> and D<sub>6</sub> by fractional crystallisation from benzene melting at 82° - 83° and 94° - 95° respectively. Fraction D<sub>5</sub> was identified as sterol. Found : C, 71.50 ; H, 10.87%. Fraction D<sub>6</sub> was insufficient for further analysis.

The acetone insoluble fraction D<sub>3</sub> containing sterol was saponified with 4% alcoholic KOH and the unsaponifiable and saponifiable portions labelled as fraction D<sub>7</sub> and D<sub>8</sub> respectively.

*Examination of unsaponifiable fraction D<sub>7</sub>:* The unsaponifiable portion was exhaustively extracted with petroleum ether and the oily residue was hydrolysed by refluxing on a water bath for 12 hours with a large excess of 20% alcoholic KOH. The crude sterol fraction was purified by chromatography of the product over Brockmann alumina using petroleum ether (b. p. 40 - 60°), petroleum ether-benzene mixture (1 : 1), benzene and ether successively as eluents. The petroleum ether-benzene fraction contained  $\gamma$ -sitosterol obtained in colourless shining plates, m. p. 138° - 40°.

*Examination of saponifiable fraction D<sub>8</sub>:* The alkaline soap solution left after petroleum ether extraction, fraction D<sub>8</sub> was acidified with 10% sulphuric acid and the liberated fatty acids were extracted with ether. The dehydrated ether extract on evaporation yielded a mixture of fatty acids, m. p. 82° - 90°; Iodine value 64.0

#### EXAMINATION OF ESSENTIAL OIL

The alcoholic extract, on evaporation under reduced pressure left a pale yellow oil, b. p. 116° - 20° having strong aromatic odour and bitter taste (Refractive index 1.4712 and sp. gr. 0.8068 at 30°; methoxy content 18.7%). It responded to tests for ketone.

#### ACKNOWLEDGMENT

The author wishes to express his grateful thanks to Prof. P. N. Wahi, M. D., M. R. C. P. (Lond.), F. N. I., Professor of Pathology and to Prof. N. K. Chowdhury, M. D., Ph. D. (Edin.), Professor of Pharmacology, Medical College, Agra for their keen interest and constant encouragement throughout these investigations.

#### REFERENCES

1. Chopra, R. N., *Indigenous Drugs of India*, Art Press, Calcutta, p. 476 (1933).
2. Kirtikar, K. R. and Basu, B. D., *Indian Medicinal Plants*, L. M. Basu, Allahabad, Vol. I, p. 76 (1935).
3. Nadkarni, K. M., *Indian Materia Medica*, Popular Book Depot, Bombay, 3rd Ed., Vol. I, p. 362 (1954).
4. Fluckiger, quoted by Dymock, *Pharmacographia Indica*, Education Society Press, Bombay, Vol. I, p. 54 (1885).

5. Pendse and Dutt, *Indian J. Med. Res.*, **20**, 663 (1932).
6. Bhide, et al., *J. Univ. Bombay*, **10**, 89 (1941).
7. Seghal, S. N. and Majumdar, D. N. *Jour. and Proc. Inst. Chem.*, **31**, 12 (1959).
8. Sylvester and Hughes, *Analyst*, **61**, 734 (1936).
9. Winter, I. B., *J. Assoc Off. Agr. Chem.*, **18**, 220-23 (1930).
10. Kolthoff, I. M., *J. Amer. Pharm. Assoc*, **17**, 360 (1928).
11. Hanak, A., *Z. Untersuch. Lebensm.*, **59**, 511 (1930).
12. Holland and Ritchie, *J. Assoc. Off. Agr. Chem.*, **22**, 333 (1937).
13. Keilin and Mann, *Biochem. J.*, **34**, 1163 (1940).

# ON THE SELF-RECIPROCAL FUNCTIONS FOR DOUBLE HANKEL TRANSFORMS

By

V. LAKSHMIKANTH

*Department of Mathematics, University College of Science, Osmania University, Hyderabad-7*

[Received on 12th October, 1959]

We know that if the function  $f(x)$  satisfies the integral equation

$$f(x) = \int_0^\infty J_p(xy) f(y) (xy)^{\frac{1}{2}} dy, \quad (1)$$

where  $J_p(x)$  is a Bessel Function of order  $p \geq -1/2$ , then  $f(x)$  is said to be a Self-Reciprocal function for Hankel Transform and is denoted by  $R_p$ .

Extending this definition we shall say that the function of two variables  $f(x_1, x_2)$  is a Self-Reciprocal function for double Hankel Transform, if it satisfies the integral equation  $f(x_1, x_2) = \int_0^\infty \int_0^\infty J_p(x_1 y_1) J_q(x_2 y_2) f(y_1, y_2) (x_1 x_2 y_1 y_2)^{\frac{1}{2}} dy_1 dy_2,$  (2)

where  $J_p(x)$ ,  $J_q(x)$  are Bessel Functions of orders  $p, q \geq -1/2$ . Let such a function be denoted by  $R_{p, q}$ .

We have immediately the following simple result :

**Theorem I:** If  $h(x_1)$  is  $R_p$  and  $g(x_2)$  is  $R_q$ , then  $f(x_1, x_2) = h(x_1) g(x_2)$  is  $R_{p, q}$ .

For, since  $h(x_1) = \int_0^\infty J_p(x_1 y_1) h(y_1) (x_1 y_1)^{\frac{1}{2}} dy_1$  and

$$g(x_2) = \int_0^\infty J_q(x_2 y_2) g(y_2) (x_2 y_2)^{\frac{1}{2}} dy_2,$$

we have  $f(x_1, x_2) = h(x_1) g(x_2) =$

$$\begin{aligned} & \int_0^\infty J_p(x_1 y_1) h(y_1) (x_1 y_1)^{\frac{1}{2}} dy_1 \int_0^\infty J_q(x_2 y_2) g(y_2) (x_2 y_2)^{\frac{1}{2}} dy_2 \\ &= \int_0^\infty \int_0^\infty J_p(x_1 y_1) J_q(x_2 y_2) h(y_1) g(y_2) (x_1 x_2 y_1 y_2)^{\frac{1}{2}} dy_1 dy_2 \\ &= \int_0^\infty \int_0^\infty J_p(x_1 y_1) J_q(x_2 y_2) f(y_1, y_2) (x_1 x_2 y_1 y_2)^{\frac{1}{2}} dy_1 dy_2 \\ &= f(x_1, x_2). \text{ Hence the result.} \end{aligned}$$

We shall now state some results for finding Self-Reciprocal functions of this type. These results are suggested by the work of Bailey [1] and Gray [5].

**Theorem II:** Suppose the function  $f(x_1, x_2)$  satisfies the integral equation

$$f(x_1, x_2) = \int_0^\infty \int_0^\infty K_1(x_1 y_1) K_2(x_2 y_2) f(y_1, y_2) dy_1 dy_2 \quad (3)$$

If  $g(x_1, x_2) = \int_a^{1/a} \int_a^{1/a} (y_1 y_2)^{-\frac{1}{2}} F(y_1, y_2) f(x_1 y_1, x_2 y_2) dy_1 dy_2$ ,  $\quad (4)$

where  $a > 0$  and  $F(x_1, x_2)$  is any function such that

$$F(x_1, x_2) = F(1/x_1, 1/x_2), \quad (5)$$

then  $g(x_1, x_2)$  also satisfies the integral equation (3)

If  $a = 0$ , we have the following general result :

**Theorem III:** Suppose the function  $f(x_1, y_2)$  satisfies the integral equation

$$f(x_1, x_2) = \int_0^\infty \int_0^\infty K_1(x_1 y_1) K_2(x_2 y_2) f(y_1, y_2) dy_1 dy_2 \quad (6)$$

Let the function  $h(x_1, x_2)$  be such that

$$(x_1 x_2)^{-\frac{1}{2}} F(x_1, x_2) = \int_0^\infty \int_0^\infty K_1(x_1 y_1) K_2(x_2 y_2) h(y_1, y_2) dy_1 dy_2 \quad (7)$$

$$(x_1 x_2)^{-\frac{1}{2}} F(1/x_1, 1/x_2) = \int_0^\infty \int_0^\infty k_1(x_1 y_1) K_4(x_2 y_2) h(y_1, y_2) dy_1 dy_2 \quad (8)$$

The function  $g(x_1, x_2) = \int_0^\infty \int_0^\infty (y_1 y_2)^{-\frac{1}{2}} F(y_1, y_2) f(x_1 y_1, x_2 y_2) dy_1 dy_2$ ,  $\quad (9)$

also satisfies the integral equation (6).

**Corollary:** If  $K_1 = K_3$  and  $K_2 = K_4$ , the above theorem reduces to a particular case of theorem II when  $a = 0$ .

The argument used in the above theorem gives the following :

**Theorem IV:** The function  $g(x_1, x_2) = \int_0^\infty \int_0^\infty f(v_1, v_2) h(x_1 u_1, x_2 u_2) dv_1 dv_2$ ,

where the function  $h$  satisfies the condition (7) and (8), also satisfies the integral equation (6).

We shall now consider a few examples on the above rules. It is known [2] that  $h(x_1) = x_1^{P+\frac{1}{2}} e^{-x_1^2/2}$  is  $R_p$  and  $g(x_2) = x_2^{q+\frac{1}{2}} e^{-x_2^2/2}$  is  $R_q$  if  $\operatorname{Re}(p)$ ,  $\operatorname{Re}(q) > -$

**Theorem I** gives that

$$f(x_1, x_2) = x_1^{P+\frac{1}{2}} x_2^{q+\frac{1}{2}} e^{-(x_1^2+x_2^2)/2} \text{ is } R_{p,q} \quad (10)$$

Putting  $p = q$ , we have  $f(x_1, x_2) = (x_1 x_2)^{P+\frac{1}{2}} e^{-(x_1^2+x_2^2)/2}$  is  $R_{p,q}$  (11)

Again if  $p = -1/2$ ,  $f(x_1, x_2) = e^{-(x_1^2+x_2^2)/2}$  (12)

is a self-reciprocal function for double Fourier transform and may be denoted by  $R_{c,c}$

Since  $h(x_1) = x_1^{-\frac{1}{2}}$  is  $R_p$ ,  $g(x_2) = J_0(ax_2) x_2^{-\frac{1}{2}}$  is  $R_1$

we have  $f(x_1, x_2) = (x_1 x_2)^{-\frac{1}{2}} J_0(ax_2)$  (13)

is  $R_{p,1}$  or  $R_{1,1}$  in particular.

We know [3] and [4] that  $h(x_1) = \frac{x_1^{P-\frac{1}{2}}}{x_1+2-2P} \frac{2}{x_1+} \frac{4-2P}{x_1+} \frac{4}{x_1+} \dots$

$= x_1^{P-\frac{1}{2}} [F(x_1)]^{-1}$  say, is  $R_p$ , if  $x_1 > 0$  and  $-1 < p < 3/2$

and  $g(x_2) = \frac{x_2^{-\frac{1}{2}}}{x_2+q+2} \frac{2}{x_2+} \frac{q+4}{x_2+} \frac{4}{x_2+} \dots = x_2^{-\frac{1}{2}} [H(x_2)]^{-1}$  say, is  $R_q$ ,

if  $q > -1$ . Hence  $f(x_1, x_2) = x_1^P (x_1 x_2)^{-\frac{1}{2}} (F(x_1) H(x_2))^{-1}$  is  $R_{p,q}$  (14)

If  $p = q = 1/2$ , (14) reduces to

$$f(x_1, x_2) = \frac{x_2^{-\frac{1}{2}}}{\left( \frac{1}{x_1+x_2} \frac{2}{x_1+x_2} \frac{3}{x_1+x_2} \frac{4}{x_1+x_2} \dots \right) \left( \frac{5}{x_2+2x_1} \frac{2}{x_2+2x_1} \frac{9}{x_2+2x_1} \frac{4}{x_2+2x_1} \dots \right)} \quad (15)$$

which is  $R_{s,s}$ .

Next we shall give some examples on Theorem II.

Taking  $f(x_1, x_2) = x_1^p x_2^q (x_1 x_2)^{\frac{1}{2}} \exp -\frac{(x_1^2+x_2^2)}{2}$  from (10), we find that

$$g(x_1, x_2) = x_1^p x_2^q (x_1 x_2)^{\frac{1}{2}} \int_a^{\infty} \int_a^{\infty} y_1^p y_2^q F(y_1 y_2) \exp -\frac{(x_1^2 y_1^2 + x_2^2 y_2^2)}{2} dy_1 dy_2 \quad (16)$$

is  $R_{p,q}$ .

Taking that  $R_{1,1}$  function (13), we find that

$$g(x_1, x_2) = (x_1 x_2)^{-\frac{1}{2}} \int_{-\infty}^{1/a} \int_{-\infty}^{1/a} (y_1 y_2)^{-\frac{1}{2}} F(y_1, y_2) J_0(ax_2 y_2) dy_1 dy_2 \quad (17)$$

is  $R_{1,1}$ . Taking  $F(x_1, x_2) = (x_1^p + x_2^{-p}) (x_1^q + x_2^{-q})$ , we get from (16)

$$\begin{aligned} g(x_1, x_2) &= x_1^p x_2^q (x_1 x_2)^{-\frac{1}{2}} \int_{-\infty}^{1/a} \int_{-\infty}^{1/a} (y_1^{2p} y_2^{2q} + y_1^{2p} + y_2^{2q} + 1) \exp \\ &\quad - \frac{(x_1^2 y_1^2 + x_2^2 y_2^2)}{2} dy_1 dy_2 \end{aligned} \quad (18)$$

which is  $R_{p,q}$ , and (17) gives, by taking  $F(x_1, x_2) = (x_1 + x_2^{-1}) (x_1 + x_2^{-1})$ , that  $g(x_1, x_2) = (x_1 x_2)^{-\frac{1}{2}} \int_{-\infty}^{1/a} \int_{-\infty}^{1/a} [(y_1 y_2)^{-2} + (y_1)^{-2} + (y_2)^{-2} + 1] J_0(ax_2 y_2) dy_1 dy_2$  is  $R_{1,1}$ . (19)

We can immediately obtain a result due to Gray [5] on Self-Reciprocal functions in double Fourier transform if we take  $K_1(x_1) = e^{2\pi i x_1}$ , and  $K_2(x_2) = e^{2\pi i x_2}$ . Then the function  $f(x_1, x_2)$  satisfying the integral equation

$$f(x_1, x_2) = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \exp[2\pi i(x_1 y_1 + x_2 y_2)] f(y_1, y_2) dy_1 dy_2 \quad (20)$$

is called a Self-Reciprocal function for double Fourier transform.

**Theorem V:** If  $f(r)$  is  $R_{4n}$ , then  $g(x_1, x_2) = r^{-\frac{1}{2}} f(r) \cos 4n\alpha$ ,

where  $r^2 = 2\pi(x_1^2 + x_2^2)$ , is a Self-Reciprocal function in the double Fourier transform.

$$\begin{aligned} \text{For } g(x_1, x_2) &= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp[2\pi i(x_1 y_1 + x_2 y_2)] g(y_1, y_2) dy_1 dy_2 \\ &= 1/2\pi \int_{0}^{\infty} \int_{-\pi}^{\pi} s^{-\frac{1}{2}} f(s) \cos 4n\beta \exp[i s \cos(\beta - \alpha)] sd\beta \end{aligned}$$

where  $s^2 = 2\pi(y_1^2 + y_2^2)$ ,  $y_1 = s \cos \beta$ ,  $y_2 = s \sin \beta$ ,  $x_1 = r \cos \alpha$  and  $x_2 = r \sin \alpha$ .

$$= \int_{0}^{\infty} s^{+\frac{1}{2}} f(s) ds 1/2\pi \int_{-\pi}^{\pi} \exp[i s \cos(\beta - \alpha)] (\cos 4n\beta) d\beta$$

$$\begin{aligned}
&= \int_0^\infty s^{\frac{1}{2}} f(s) ds \cdot \frac{1}{2\pi} \int_0^\infty e^{-\frac{\pi \operatorname{ins} \cos v}{4n}} \cos 4n(v + \infty) dv \\
&= \int_0^\infty s^{\frac{1}{2}} f(s) ds \cdot \frac{1}{\pi} \int_0^\infty e^{-\frac{\pi \operatorname{ins} \cos v}{4n}} \cos 4nv \cos 4n \infty dv \\
&= \int_0^\infty J_{4n}(rs) f(s) (rs)^{\frac{1}{2}} r^{-\frac{1}{2}} \cos 4n \infty ds \\
&= f(r) r^{-\frac{1}{2}} \cos 4n \infty = g(x_1, x_2).
\end{aligned}$$

Since  $\pi J_{4n}(rs) = \int_0^\infty e^{-\frac{\pi \operatorname{ins} \cos v}{4n}} \cos 4nv dv$ . cf. [6]

Hence the result.

Finally, we can restate theorem IV as

**Theorem IV (A):** If  $f(x_1, x_2)$  is  $R_{p, q}$  and  $h(x_1, x_2)$  is such that its reciprocal  $(p, q)$  is  $(x_1 x_2)^{-\frac{1}{2}} F(x_1, x_2)$  while its reciprocal  $(\alpha, \beta)$

is  $(x_1 x_2)^{-\frac{1}{2}} F(1/x_1, 1/x_2)$ , then the function

$$g(x_1, x_2) = \int_0^\infty \int_0^\infty f(y_1, y_2) h(x_1 y_1, x_2 y_2) dy_1 dy_2 \quad (21)$$

is  $R_{\alpha, \beta}$ . Also, if  $f(x_1, x_2)$  is  $R_{\alpha, \beta}$ ,  $g(x_1, x_2)$  is  $R_{p, q}$ .

#### REFERENCES

1. Bailey, W. N.: (1931) On the solutions of some integral equations, *Jr. of the Lond. Math. Soc.*, Vol 6, pp. 242-247.
2. Do. : (1930) On a function which is its own reciprocal in the Fourier Bessel integral transform, *Ibid.*, Vol. 5, pp. 92-95.
3. Do. : (1930) A generalisation of an integral due to Ramanujan, *Ibid.*, Vol. 5, pp. 200-202.
4. Do. : (1931) A note on an integral due to Ramanujan, *Ibid.*, Vol. 6, pp. 216-17.
5. Gray, M. C.: (1931) Note on some Self-Reciprocal functions in the double Fourier transform, *Ibid.*, Vol. 6, pp. 247-250.
6. Watson, G. N.: (1922) Theory of Bessel Functions (Cambridge) p. 124,

# STUDIES ON THIOSALTS -PART I

## FORMATION OF THIOSALT FROM MERCURIC SULPHIDE

By

KESHAVA PRASAD DUBEY and SATYESHWAR GHOSH

*Chemical Laboratories, University of Allahabad, Allahabad*

### ABSTRACT

The paper deals with the dissolution of mercuric sulphide in alkaline sulphides. It is confirmed that the compound  $\text{Na}_2\text{HgS}_2$  is formed and the stability constant of the complex anion has been determined. The formation of the complex anion is complete in alkaline sulphide containing a large excess of free alkali.

Mercuric sulphide is known to dissolve in alkali sulphide and Knox<sup>1</sup> reported that the solubility of the sulphide is greater in potassium sulphide than in sodium sulphide. The dissolution of mercuric sulphide in alkaline sulphide is ascribed to the formation of a thiosalt, from which the mercuric sulphide is precipitated by either diluting the solution with water or making it less alkaline by adding ammonium chloride, sodium bicarbonate or sodium dihydrogen phosphate or an acid.<sup>2</sup> Recently, Martin<sup>3</sup> and Akobajnoff<sup>4</sup> reported that in presence of a large excess of caustic soda, mercuric sulphide dissolves in sodium sulphide forming a complex of the formula  $(\text{NaS})_2\text{Hg}$ . A method for the estimation of mercury based on the formation of its thiosalt and its subsequent decomposition into the sulphide has been also developed in these laboratories.<sup>5</sup> An excess of sodium sulphide is added to a mercuric salt solution till the formation of the thiosalt is complete. This is followed by the addition of dilute hydrochloric acid in excess to decompose the thiosalt. The solution is boiled and the precipitate is filtered through a sintered glass crucible, washed with hot water and finally with absolute alcohol and ether, dried at 105°C, cooled and weighed as mercuric sulphide. Salaria<sup>6</sup> continuing the same work has also reported complete precipitation of mercuric sulphide from the thiosalt by the addition of excess of ammonium acetate.

The present paper deals the study of the dissolution of mercuric sulphide in alkaline solution and with the calculation of the stability constant of the thiosalt formed by the solubility of mercuric sulphide in alkaline medium.

### EXPRIMENTAL

To 100 c.c. of standardised sodium or potassium hydroxide solution purified hydrogen sulphide was passed for about 20-25 minutes. The sulphide in solution was estimated iodimetrically. To this solution calculated amount of alkali hydroxide solution was added so that the ratio of sulphur to alkali hydroxide is 1:2. The solutions thus prepared were used in the following experiments. In every case freshly prepared solutions were used, as on keeping the solutions are likely to be oxidised.

About 30 grams of mercuric chloride of reagent grade were dissolved in hot water and then made upto a litre, so that the solution was approximately 0.1 molar. The solution was finally standardised by the decomposition of the thiosalt.

In all the solubility experiments the reaction mixtures were prepared in 250 c.c. bottles. They were thoroughly shaken with the help of an electric shaker for about an hour and then kept overnight. Next day 10 c.c. of the supernatant

solution was pipetted out and the solution made acidic by adding an excess of 2N hydrochloric acid. This treatment decomposed all the thiosalt present in solution, into mercuric sulphide, which was estimated as already described. The results obtained are given below.

In table I the observations on the formation of thiosalt of mercury in presence of a large excess of alkali are recorded. To a constant amount of mercuric chloride solution different quantities of potassium sulphide, in the presence of excess of potassium hydroxide are added. The amount of  $S^{2-}$  anion in gms. reacting to form mercuric sulphide is noted in col. (5) of the table. In col. 6 of the table the  $S^{2-}$  the total sulphide, both in excess and in combination with mercuric sulphide to form the complex, is noted in gm moles. Col. 7 gives the amount of mercuric sulphide in gm moles dissolved in the solution. The last column gives the ratio, of mercuric sulphide in solution to the amount of the sulphide (free or combined) left over, after the formation of mercuric sulphide.

It is seen from the table I that in presence of large excess of an alkali, practically the whole amount of sulphide left over after the formation of mercuric sulphide has combined with mercuric sulphide. The ratio given in col. 9 approaches the value of 1:1. In other words, the amount of mercuric sulphide in solution is nearly equal to the sulphide left over in the solution. This confirms the formation of the compound  $Na_2HgS_2$ , which tends to complete in increasing amount of potassium hydroxide.

In table II the formation of thiosalt in sodium sulphide solution alone is given. It will be seen that a large excess of sodium sulphide remains free in the solution, which is calculated as the difference of the total sodium sulphide added, and the sulphide consumed in the formation of mercuric sulphide and the complex of the formula  $Na_2HgS_2$ .

It will be interesting to find in table II that the concentration of the anion  $(HgS_2)^{-2}$  and the  $S^{2-}$  remaining free in the solution bear a relation, which is approximately constant. The concentration of the anion sulphide remaining free in the solution has been calculated as usual from the knowledge of the dissociation constants of hydrogen sulphide.

Table III contains similar experimental data as has been described in table II Only sodium sulphide has been replaced by potassium sulphide.

The results in table III show that the ratio of the anion  $(HgS_2)^{-2}$  to the anion  $S^{2-}$ , as calculated from the excess of potassium sulphide present in the solution is approximately constant. These values are not much different from those given in table II. where the solubility of mercuric sulphide in sodium sulphide has been investigated.

In table IV the dissolution of mercuric sulphide in sodium sulphide has been studied by adding sodium hydroxide in varying amounts. The variation in  $OH^-$  ion concentration is comparatively small.

From table IV we find the ratio of  $(HgS_2)^{-2}$  to  $S^{2-}$  to be approximately constant and very near to the values obtained in tables II and III. The  $S^{2-}$  has been calculated from the knowledge of hydrolysis constant of sodium sulphide, which is remaining free in the system in equilibrium with the  $OH^-$  ions added to the solution.

TABLE I  
 1.  $K_2S$  and KOH mixture, containing 25 c.c. of 0·7688 N  $K_2S$  with 100 c.c. of 7·5 N KOH in 125 c.c.  
 2. Mercuric chloride 0·1352N

	1	2	3	4	5	6	7	8	9
$HgCl_2$ c.c.	$S^{2-}, OH^-$ mix. c.c.	Total vol. c.c.	S added gms.	S consumed in $HgS$ gms.	$K_2S$ re- main- ing M	$HgS$ dissolved M	$OH^-$ present M	$HgS$ dissolved $S^{2-}$ in solution	
10	10	20	0·04920	0·04320	0·009378	0·007761	3·000	0·828	
10	12	22	0·05904	0·04320	0·02251	0·02147	3·273	0·954	
10	14	24	0·06888	0·04320	0·03344	0·03235	3·500	0·9822	
10	15	25	0·07380	0·04320	0·03825	0·03521	3·599	0·9464	
10	16	26	0·07872	0·04320	0·04269	0·04094	3·693	0·9590	
10	18	28	0·08856	0·04320	0·05063	0·04724	3·857	0·933	

TABLE II  
 1. Sodium sulphide 0·3765 M.  
 2. Mercuric chloride 0·1142 M.

	1	2	3	4	5	6	7	8	9	10
$HgCl_2$ c.c.	$Na_2S$ c.c.	Total vol. c.c.	$S^{2-}$ added in gms.	$S^{2-}$ used in $HgS$ gms.	$Na_2S$ remain- ing molar	$[HgS_2]^{2-}$ formed molar	$Na_2S$ remain- ing after the formation of $HgS_2$	$S^{2-}$ present in (8) $Na_2S$ molar,	$[HgS_2]^{2-}$ $[S^{2-}]$	
10	10·0	20·0	0·1205	0·03654	0·1312	0·01526	0·1159	0·00160	9·5	
10	12·5	22·5	0·1506	0·03654	0·1585	0·02310	0·1354	0·00220	10·5	
10	15·0	25·0	0·1807	0·03654	0·1803	0·02914	0·1512	0·00269	10·8	
10	17·5	27·5	0·2109	0·03654	0·1982	0·03360	0·1596	0·00301	12·5	

TABLE III  
 1. Potassium sulphide 0·3790 N  
 2. Mercuric chloride 0·1142 N

1	2	3	4	5	6	7	8	9	10
HgCl <sub>2</sub> c.c.	Na <sub>2</sub> S c.c.	Total vol. c.c.	S <sup>2-</sup> added in gms.	S <sup>2-</sup> used in HgS molar	K <sub>2</sub> S remaining molar	[HgS <sub>2</sub> ] <sup>2-</sup> formed molar	K <sub>2</sub> S remain- ing after the formation in (8) K <sub>2</sub> S of HgS <sub>2</sub> molar	[HgS <sub>2</sub> ] <sup>2-</sup> present [S <sup>2-</sup> ] molar	
10	3·5	13·5	0·04346	0·03654	0·01601	0·0000	0·01601	0·00006	...
10	6·0	16·0	0·07278	0·03654	0·07079	0·005443	0·06535	0·00050	10·9
10	10·0	20·0	0·1213	0·03654	0·1324	0·01905	0·1133	0·00140	13·6
10	12·0	22·0	0·1456	0·03654	0·1548	0·02345	0·1313	0·00195	12·0
10	12·5	22·5	0·1516	0·03654	0·1599	0·02664	0·1333	0·00210	12·7
10	14·0	24·0	0·1698	0·03654	0·1736	0·03206	0·1415	0·00230	13·9

TABLE IV

1. Sodium sulphide 0·3765 N
2. Sodium hydroxide 0·7536 N
3. Mercuric chloride 0·1142 N

1	2	3	4	5	6	7	8	9	10
HgCl <sub>2</sub> c.c.	Na <sub>2</sub> S c.c.	Na OH c.c.	Total vol. c.c.	Na <sub>2</sub> S left after the formation of HgS molar	[HgS <sub>2</sub> ] <sup>2-</sup> formed M	Na <sub>2</sub> S free in OH' added solution M	Na <sub>2</sub> S in free solution M	Na <sub>2</sub> S M	[HgS <sub>2</sub> ] <sup>2-</sup> [S <sup>2-</sup> ]
10	5	30	45	0·01646	0·005517	0·01094	0·5023	0·00059	9·4
10	6	29	45	0·02490	0·008839	0·01606	0·4854	0·00086	10·3
10	7	28	45	0·03320	0·01277	0·02047	0·4688	0·00162	7·9
10	8	27	45	0·04158	0·01651	0·02507	0·4522	0·00127	13·0

In table V the results obtained for the dissolution of mercuric sulphide in a constant amount of sodium sulphide in the presence of different quantities of alkali in solution are given.

TABLE V

1. Sodium sulphide 4 c. c. containing 0·1268 gms. of S and 0·16 gms. NaOH
2. Sodium hydroxide 8·92 N
3. Mercuric chloride 17·3 c. c. (0·06855 N) to give 0·4602 gm. HgS.

NaOH in c. c.	Total volume c. c.	Na <sub>2</sub> S left after the formation of HgS molar	[HgS <sub>2</sub> ] <sup>-2</sup> formed molar	OH' added molar
1	29·3	0·06751	0·01462	0·1708
2	29·3	0·06751	0·02833	0·4758
4	29·3	0·06751	0·04303	1·085
6	29·3	0·06751	0·04897	1·696
8	29·3	0·06751	0·05379	2·306

The above results are represented in figure 1 where the amount of  $(\text{HgS}_2)^{-2}$  formed is plotted against the OH' added in the solution. It may be con-

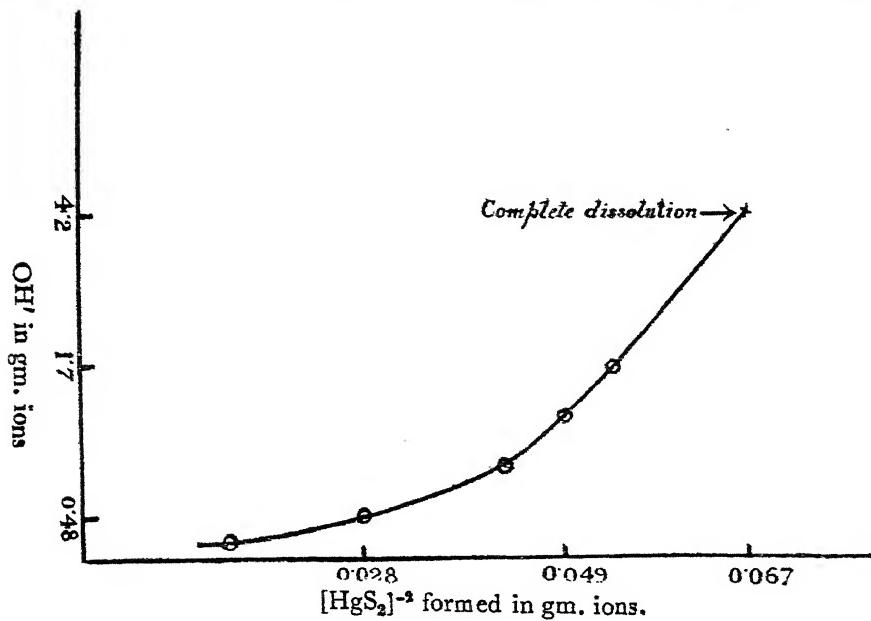
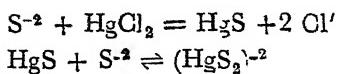


Fig. 1.

cluded from the graph that the complete dissolution of 0·06751 M of Mercuric sulphide takes place in a litre of solution containing 0·06751 molar of sodium sulphide in the presence of 4·16 M of sodium hydroxide.

## CONCLUSION

The experimental results given in earlier tables in this paper show that when sodium sulphide solution is added to a mercuric chloride solution the following reactions take place:

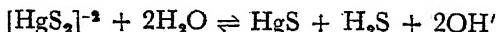


Since mercuric sulphide is insoluble we may take its effective mass remaining constant and from the equation to we find,

$$\frac{\text{Concentration of } HgS_2^{-2}}{\text{Concentration of } S^{2-}} = K$$

Where K is the stability constant of the complex formed. It is interesting to note that the stability constant is practically the same for the two alkali sulphides,  $Na_2S$  and  $K_2S$ . In other words, our results show that the solubility of the mercuric sulphide forming the thiosalt is same for potassium and sodium sulphides.

It has been noted in this paper that  $OH^-$  ions play a great role in the formation of the thiosalt, so much so, that on increasing concentration of alkali greater amount of mercuric sulphide goes in solution. It is clear, therefore, that the solubility of mercuric sulphide forming the thiosalt is related to the following equilibrium :



The excess of alkali suppresses the above hydrolysis, as well as the hydrolysis of sodium sulphide producing more sulphide anions in the solution. Both these factors account for the increased solubility of mercuric sulphide in alkaline sodium sulphide solution.

Further work is in progress and the results will be communicated in the next paper.

## REFERENCES

1. Knox, J. *vide* Mellor, J. W., Treatise on Inorganic and Theoretical Chemistry, London, 4, 953 (1923)
2. Berthelot, M., *ibid.*, 4, 953 (1923)
3. Martin, Geo. E. *Chemical Abstracts.* 41 (2), 4816d (1950)
4. Akobajnoff, Lev., *ibid.*, 47 (3), 8088h (1953)
5. Taimni, I. K. and Salaria, G. B. S., *Anal. Chim. Acta*, 12, 522 (1952)
6. Salaria, G. B. S., *ibid.*, 15, 516 (1956)

## STUDIES ON THIOSALTS—PART II

### CONDUCTOMETRIC STUDY OF MERCURIC THIOSALT

By

KESHAVA PRASAD DUBEY and SATYESHWAR GHOSH

*Chemical Laboratories, University of Allahabad, Allahabad*

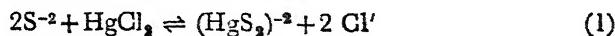
[Received on 5th October 1959]

#### ABSTRACT

In part I of this series<sup>1</sup> the stability constant of the mercuric thiosalt formed by the dissolution of mercuric sulphide by an alkali sulphide has been determined by the solubility method. The present paper deals with the conductometric study of the formation of this salt of mercury. It has been shown that the thiosalt hydrolyses and its hydrolysis constant has been calculated. This gives an idea of the strength of the thioacid of mercury. It is found that the acid is very weak, but stronger than hydrogen sulphide.

The preparation and standardisation of sodium sulphide, mercuric chloride solutions are as described in part I of this series. In conductometric titration 5 c. c. s. of (0.09615M) sodium sulphide were taken in 50 c. c. measuring flasks. To these varying amounts of mercuric chloride (0.1142 M) were added, and then their volumes were made up to 50 c. c. s. in each case. These were well shaken and kept in a thermostat at 32°C. After an hour the conductance of the solutions were measured at the same temperature. The observed conductivities for the varying amounts of mercuric chloride added are shown in figure 1.

As mercuric chloride is progressively added to the sodium sulphide solution the electrical conductivity continuously goes on decreasing upto C, but there are two breaks in the regular curve at the points A and B. It has been noted that upto the point A the solution remains colourless i. e. all mercuric sulphide formed completely dissolves in the sodium sulphide solution. Beyond A a black precipitate appears and continues to be formed in greater quantities upto B. After B the precipitate becomes more copious till the point C is reached, beyond which the electrical conductivity increases and tends to become constant. This shows that upto the point A the complex anion  $[\text{HgS}_2]^{2-}$  is formed by the complete dissolution of mercuric sulphide according to the equation :

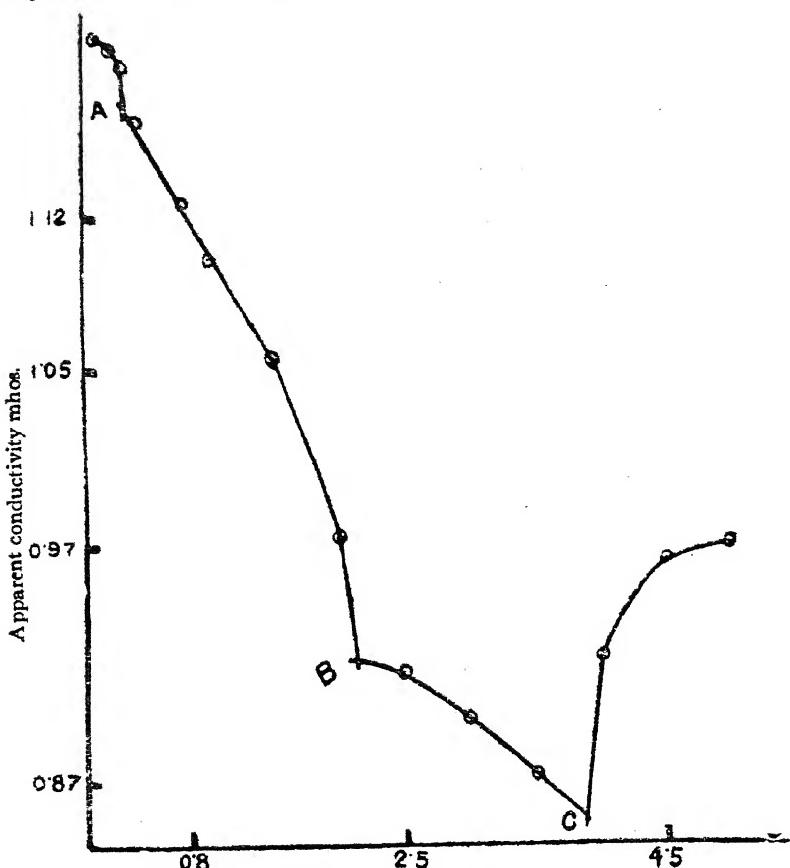


Two sulphide ions lead to the formation of the complex anion and two chloride ions liberated. This should lead to increased electrical conductivity but the decrease in conductance is rapid. Hence the decrease is chiefly due to the removal of highly conducting OH' ions occurring in solution because of following equilibrium :—



Further hydrolysis of HS' ions forming OH' and H<sub>2</sub>S is negligible as compared with the hydrolysis of sulphide anion. Hence, when sulphide ions react with mercuric chloride to produce mercuric sulphide and then the complex anion  $[\text{HgS}_2]^{2-}$  the equilibrium (2) will be displaced and a decrease in OH' ions will lead to a rapid decrease in electrical conductance of sodium sulphide solution.

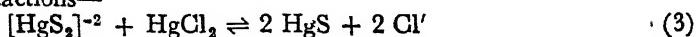
Beyond A the decrease in electrical conductivity continues but mercuric sulphide is not completely dissolved in excess sodium sulphide present. It is clear that some complex of mercuric sulphide is formed but the whole amount of mercuric



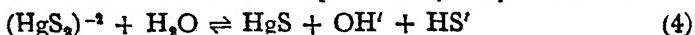
Mercuric chloride added in c. c. s.

Fig. 1.

sulphide formed is not completely converted into the complex. This continues upto the point B, which contains approximately two equivalents of sodium sulphide to which one equivalent of mercuric chloride has been added. If the complex anion were very stable the one equivalent amount of mercuric chloride forming mercuric sulphide should have completely dissolved to yield  $[HgS_2]^{-2}$ . The decrease in electrical conductance is due also to the removal of  $OH^-$  ions during the whole process occurring between A and B. In this region we may expect the following reactions—

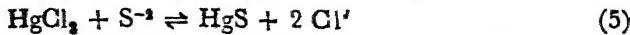


The reaction (3) cannot explain the decrease in electrical conductance unless we consider that the thioanion is also capable to hydrolyse as follows :—



In the above equation the mercuric sulphide formed by the addition of mercuric chloride may remove some  $OH^-$  ions from the system by forming the complex anion  $(HgS_2)^{-2}$ .

After we have attained the ratio of  $S^{-2}$  to  $Hg^{+2}$  to 2:1 i.e., at the point B all the sulphide ions should be consumed by the formation of  $HgS_2^{-2}$  and therefore from the point B onwards the precipitation of mercuric sulphide occurs partly according to the equations (3) and (4) and mainly according to the following equation :—



the sulphide ions being obtained from the hydrolysis of thiosalt. It is clear from the equation (4) that the concentration of  $HgS_2^{-2}$  anion in solution is directly related to the concentration of  $OH'$  ions in this system. This has been shown to take place in our earlier paper.<sup>1</sup> This means that there must be a minimum amount of  $OH'$  ions in the system to start the formation of the complex anion  $HgS_2^{-2}$ . It appears that at the point B this minimum amount of  $OH'$  ion concentration is obtained and, therefore, further addition of mercuric chloride results only in the formation of mercuric sulphide and not the thiosalt. The slope BC shows fall in conductivity due to the replacement of  $OH'$  ions by  $Cl'$  ions. But here the slope is less steeper than the earlier slopes. It is because in equation (5) one  $S^{-2}$  ion is reacting to give two  $Cl'$  ions, whereas earlier slopes represented mainly the equation (1) in which two  $S^{-2}$  ions were being replaced by two  $Cl'$  ions. As the  $S^{-2}$  ion concentration is directly proportional to  $OH'$  ion concentration, for the earlier stages two  $OH'$  ions were being replaced by two  $Cl'^{-}$  ions and later stage represented by BC one  $OH'$  ion is being replaced by two  $Cl'$  ions.

When the point C is reached the ratio of S to Hg is 1:1 and therefore it represents the point of this reaction where all mercury has precipitated as mercuric sulphide.

The further addition of mercuric chloride first causes a little increase in conductivity possibly due to an increase in the hydrogen ion concentration obtained from some free hydrochloric acid in mercuric chloride. The conductance of the solution finally tends to become constant because mercuric chloride solution is a poor conductor of electricity.

It will be now interesting to investigate the reaction (4) pertaining to the hydrolysis of the thioanion  $[HgS_2^{-2}]$ . By taking the effective mass of mercuric sulphide to be constant we can write the equation as follows :—

$$\frac{(OH') \times (HS)}{(HgS_2)^{-2}} = k_h \quad (6)$$

This  $k_h$  is the hydrolysis constant of the anion  $HgS_2^{-2}$ . This value for  $k_h$  can be obtained from the knowledge of hydrolysis constant sodium sulphide calculated from the dissociation constant of hydrogen sulphide. Thus

$$\frac{(OH) \times (HS)}{S^{-2}} = 8.333 \quad (7)$$

The value of stability constant of the anion  $(HgS_2)^{-2}$  has been determined by us and found to be

$$\frac{(HgS_2)^{-2}}{S^{-2}} = 12 \quad (8)$$

Therefore, the value of  $K_h$  is

$$\frac{8.333}{12} = 0.6944 \quad (9)$$

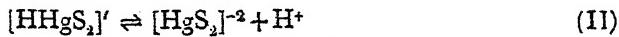
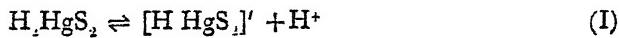
With this hydrolysis constant for the anion  $(HgS_2)^{-2}$  the amount of alkali required to be present so that 99% of 0.0048 gm moles of the thio-anion are hydrolysed

is calculated to be the pH 11.65. At the point B, the excess of sodium sulphide is 0.0048 gm moles which on hydrolysis yields OH' ions equivalent to pH 11.68. In other words, we can say that the thiosalt had completely hydrolysed at the pH 11.68 which leads to the conclusion that below this pH the formation of the thiosalt is not possible. The part BC of the curve therefore represents only the precipitation of mercuric sulphide.

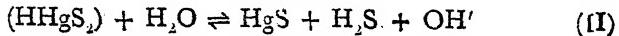
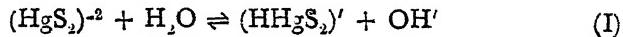
From the equation (9) the values of pH at which the given amount of thiosalt will remain with negligible hydrolysis in a sodium sulphide solution are calculated.

gm moles of $[HgS_2]^{-2}$	pH of $Na_2S$ solution
1.00000	13.93
0.10000	13.40
0.01000	12.90
0.00100	12.40
0.00010	11.90
0.00005	11.65

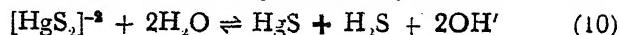
The thiosalt of mercury  $Na_2(HgS_2)$  which has been under investigation is a salt of thioacid  $H_2(HgS_2)$ , the dissociation of which can be suggested to take place in two steps



The hydrolysis of the complex anion also takes place in two steps as noted below :—



The hydrolysis constant for the complete hydrolysis of the thiosalt is given by



and the constant  $K_h$  is given by

$$\frac{K_w^2}{k_1 k_2} = K_h \quad (11)$$

While  $k_1$  and  $k_2$  are the two dissociation constants of the thioacid and  $K_h$  the hydrolysis constant for the relation

$$\frac{(OH)^2 \times (H_2S)}{(HgS_2)^{-2}} \quad (12)$$

The same relation can be obtained from the following equation

$$\frac{K_w^2}{K_1 K_2 K_h} = K_h \quad (13)$$

The  $K_1$  and  $K_2$  being dissociation constants of hydrogen sulphide and  $K_h$  the stability constant of the mercuric thioanion. Therefore,

$$\frac{K_w^2}{k_1 k_2} = \frac{K_w^2}{K_1 K_2 K_s} \quad (14)$$

and finally

$$\begin{aligned} k_1 k_2 &= K_1 K_2 K_s \\ &= 1.2 \times 9.1 \times 10^{-12} \times 12 \\ &= 1.31 \times 10^{-11} \end{aligned} \quad (15)$$

Thus we find that the product of the two dissociation constants of the thioacid  $H_2HgS_2$  is  $1.31 \times 10^{-11}$ , whereas the product of the two dissociation constants of hydrogen sulphide is  $1.092 \times 10^{-12}$ . The comparison shows that this thioacid though very weak is yet 12 times stronger than hydrogen sulphide.

Further work is in progress and the results will be communicated in due course.

#### REFERENCE

1. Dubey K. P. and Ghosh, S., *Proc. Nat. Acad. Sci., India*, **29A**, 301, (1959)

# A NOTE ON SELF-RECIPROCAL FUNCTIONS

By

V. LAKSHMIKANTH

*Department of Mathematics, University College of Science, Osmania University,  
Hyderabad, Deccan-7.*

[Received on 12th October, 1959]

Let the function  $f(x)$  satisfy the homogeneous integral equation

$$f(x) = \int_0^\infty J_p(xy) (xy)^{\frac{1}{2}} f(y) dy, \quad (1)$$

where  $J_p(x)$  is a Bessel Function of order  $p \geq -1/2$ . Then, in the notation of Hardy and Titchmarsh [1],  $f(x)$  is called a Self-Reciprocal function of order  $p$  and is denoted by  $R_p$ .

We shall prove the following result.

**Theorem I:**

Let  $f_1(x), f_2(x), \dots, f_n(x)$  be a system of  $R_p$  functions than the function

$$g(x, t) = \sum_{i=1}^n h_i(t) f_i(x h_i^{-2k}(t)) \sum_{i=1}^n h_i^{-k}(t) f_i(x h_i^{-2k}(t)) \quad (2)$$

is also  $R_p$  for every fixed  $t$  and every real number  $k$ , provided the functions  $h_i(t) > 0$  for all  $t$ .

$$\begin{aligned} \text{Proof: } & \text{For } \int_0^\infty J_p(xy) (xy)^{\frac{1}{2}} g(t, y) dy = \\ & \int_0^\infty J_p(xy) (xy)^{\frac{1}{2}} \left[ \sum_{i=1}^n h_i(t) f_i(y h_i^{-2k}(t)) + \sum_{i=1}^n h_i^{-k}(t) f_i(y h_i^{-2k}(t)) \right] dy \\ & = \int_0^\infty J_p(xy) (xy)^{\frac{1}{2}} \sum_{i=1}^n h_i(t) f_i(y h_i^{-2k}(t)) dy + \int_0^\infty J_p(xy) (xy)^{\frac{1}{2}} \sum_{i=1}^n h_i^{-k}(t) f_i \\ & \quad (y h_i^{-2k}(t)) dy \\ & = I_1 + I_2 \text{ say.} \end{aligned} \quad (3)$$

Applying the transformation  $u_i = y h_i^{-2k}(t)$  and  $v_i = y h_i^{-2k}(t)$  to  $I_1$  and  $I_2$  of (3) respectively, we obtain

$$I_1 + I_2 = \sum_{i=1}^n h_i^{-k}(t) \int_0^\infty J_p(x h_i^{-2k}(t) u_i) (x h_i^{-2k}(t) u_i)^{\frac{1}{2}} f_i(u_i) du_i$$

$$\begin{aligned}
& + \sum_{i=2}^n h_1(t) \int_0^\infty J_p(x h_1(t), \tau_i)^{-2k} f_1(\tau_i)^{\frac{1}{2}} d\tau_i \\
& = \sum_{i=1}^n h_1(t) f_1(x h_1(t))^{-2k} + \sum_{i=1}^n h_1(t) f_1(x h_1(t)) = g(x, t),
\end{aligned} \tag{4}$$

since the functions  $f_1(x)$  are self-reciprocal by assumption. Hence the result is proved.

Brij Mohan [2] and [3] has shown that

$$g(x) = h(a) f(x h^2(a)) + h^{-1}(a) f(x h^{-2}(a)) \quad \text{and}$$

$$g(x) = a^n f(x a^{2n}) + a^{-n} f(x a^{-2n}) \text{ are } R_p \text{ functions,}$$

if  $f(x)$  is  $R_p$ . Obviously, these are particular cases of Theorem I. For, taking  $n = 1, k = 1$  and  $t = a$  in (2) we get the former and if  $h(t) = t^n$ , the latter is obtained.

Extending this definition (1), we shall say that a function of two variables  $f(x, y)$  is a self-reciprocal function for double Hankel transform, if it satisfies the integral equation

$$f(x, y) = \int_0^\infty \int_0^\infty J_p(xy) J_q(ys) (xys)^{\frac{1}{2}} f(t, s) dt ds, \tag{5}$$

where  $J_p(x)$ ,  $J_q(x)$  are Bessel Functions of order  $p, q \geq -1/2$ . We shall denote such a function by  $R_{p, q}$ .

The following is the corresponding result of Theorem I.

**Theorem II:** Let  $f_1(x, y), f_2(x, y), \dots, f_n(x, y)$  be a system of  $R_{p, q}$  functions. Then the function

$$\begin{aligned}
g(x, y, t) &= \sum_{i=1}^n p_1(t) q_1(t) f_1(x p_1(t), y q_1(t)) \\
& + \sum_{i=1}^n p_1(t) q_1(t) f_1(x p_1(t), y q_1(t))
\end{aligned} \tag{6}$$

is  $R_{p, q}$  for every fixed  $t$  and every real number  $k$ , provided the functions  $p_1(t), q_1(t) \geq 0$  for all  $t$ .

The proof is similar to the proof of Theorem I.

Some examples may be considered now.

Taking  $f_1(x) = x^{-\frac{1}{2}}$

$$f_2(x) = x^{P+\frac{1}{2}} e^{-x^2/2}$$

$$f_3(x) = x^{P+\frac{1}{2}} e^{-x^2/2} {}_1F_1(-2n; 1+p/2 - n; 1/2 x^2)$$

(where  $n$  is a positive integer)

which are known [4] to be  $R_p$  functions, we obtain from (2) for  $t = a$  that

$$g'(x) = h_1^{-k}(a) (x h_1^{-2k}(a))^{-\frac{1}{2}} + h_1^{-k}(a) (x h_1^{-2k}(a))^{-\frac{1}{2}} + h_2^{-k}$$

$$(a) (x h_2^{-2k}(a))^{P+\frac{1}{2}} e^{-[x h_2^{-2k}(a)]^2/2}$$

$$+ h_2^{-k}(a) (x h_2^{-2k}(a))^{P+\frac{1}{2}} e^{-[x h_2^{-2k}(a)]^2/2} + h_3^{-k}(a) (x h_3^{-2k}(a))^{P+\frac{1}{2}}$$

$$+ [x h_3^{-2k}(a)]/2 {}_1F_1(-2n; 1+p/2 - n; 1/2 (x h_3^{-2k}(a))^2)$$

$$+ h_3^{-k}(a) (x h_3^{-2k}(a))^{P+\frac{1}{2}} e^{-[x h_3^{-2k}(a)]^2/2}$$

${}_1F_1(-2n; 1+p/2 - n; 1/2 (x h_3^{-2k}(a))^2)$  is  $R_p$

It is known [5] that  $\sum_{i=1}^n J_{p_i}(a_i x) x^{-\sum p_i} x^{-\frac{1}{2}}$  is  $R_1$  if  $a_i > 0$  and  $\sum a_i < x$ .  
 $-(p_1 + \frac{1}{2})$

$$\text{Hence } f_1(x) = J_{p_1}(a_1 x) x^{-(p_1 + p_2 + \frac{1}{2})}$$

$$f_2(x) = J_{p_2}(a_2 x) J_{p_1}(a_1 x) x$$

.....

$$f_n(x) = \frac{n}{\pi} J_{p_1}(a_1 x) x^{\sum_{i=1}^n p_i - \frac{1}{2}}$$

is a system of  $R_1$  functions. We therefore obtain from (2) for

$t = a$  that

$$g(x) = h_1^{-k}(a) J_{p_1}(a_1 x h_1^{-2k}(a)) (x h_1^{-2k}(a))^{-(p_1 + \frac{1}{2})} + h_1^{-k}(a) J_{p_1}(a_1 x h_1^{-2k}(a))$$

$$+ (x h_1^{-2k}(a))^{-(p_1 + \frac{1}{2})}$$

$$+ \dots + \dots + \dots + \dots + \dots$$

$$+ \frac{h}{n}^k (a) J_{p_1}(a_1 x h_n - (a)) J_{p_2}(a_2 x h_n - (a)) \dots J_{p_n}(a_n x h_n - (a)) (x h_n - (a))^{-(\sum p_i + \frac{1}{2})}$$

$$+ \frac{-h}{n} (a) J_{p_1}(a_1 x h_n - (a)) J_{p_2}(a_2 x h_n - (a)) \dots J_{p_n}(a_n x h_n - (a)) (x h(a))^{-(\sum p_i + \frac{1}{2})}$$

is an  $R_{p,1}$  function.

$$\text{Taking } f_1(x, y) = x^{p+\frac{1}{2}} y^{3/2} e^{-(x^2+y^2)/2},$$

$$f_2(x, y) = (xy)^{-\frac{1}{2}} J_0(ay),$$

which are known [6] to be  $R_{p,1}$  functions, we get from (6) for  $t = a, t = b$  that

$$g(x, y) = p_1(a) q_1(b) (xp_1(a))^{-2k} (yq_1(b))^{-3/2} \exp[-\frac{1}{2}(xp_1(a) + yq_1(b))] \\ + p_1(a) q_1(b) (xp_1(a))^{-2k} (yq_1(b))^{-3/2} \exp[-1/2(xp_1(a) + yq_1(b))] \\ + p_1(a) q_1(b) (xp_1(a))^{-\frac{1}{2}} (yq_1(b))^{-\frac{1}{2}} J_0(ayq_1(b)) + \\ + p_1(a) q_1(b) (xp_1(a))^{-2k} (yq_1(b))^{-2k} J_0(ayq_1(b)) \text{ is an } R_{p,1} \text{ function.}$$

#### REFERENCES

1. Hardy, G. H. and Titchmarsh, E. C. : (1930). 'Self Reciprocal Functions', *Quart. Jour. Maths.* (Oxford Series), Vol. I, page 196.
2. Brijmohan (1934). 'A few self-reciprocal functions', *Proc physico Math. Soc. Japan.*
3. do (1939). 'A note on self-reciprocal functions', *Current Science*, Vol. 8, page 207.
4. Bailey, W. N. (1930). 'Some Classes of functions which are their own reciprocals in the Fourier-Bessel Integral Transform', *Jour. Lond. Math. Soc.*, Vol. 5, p. 258.
5. Rao, V. V. L. N. : (1957). 'On self-reciprocal functions', *Proc. Nat. Acad. Sci. (India)*, 26-A, p-135.
6. Lakshmikantham, V. "On the self-reciprocal functions for double Hankel Transform" (Submitted for publication).

# STUDIES ON THE MUTUAL COAGULATION OF SOLS

## PART I—CHANGES IN THE CONDUCTIVITY OF COPPER FERROCYANIDE SOL BY THE GRADUAL ADDITION OF HYDROUS OXIDE SOLS OF ALUMINIUM AND CHROMIUM

By

MIRZA AIJAZ BEG and WAHID U. MALIK

*Department of Chemistry, Muslim University, Aligarh*

[Received on 24th June, 1959]

### SUMMARY

Mutual coagulation of copper ferrocyanide sols containing varying amounts of the peptising electrolyte by hydroxide sols of aluminium and chromium have been studied both for the fresh and aged sols. For aluminium hydroxide sol the results indicate that the contra ions are continuously liberated in different zones of mutual coagulation. The conductivity measurements with chromium hydroxide sol show that besides the liberation of the contra ion, the liberated contra ions are simultaneously adsorbed. Neither ageing of the sol nor the variation in the amount of the peptising electrolyte influence the nature of the conductance changes.

The first systematic study on the mutual coagulation of oppositely charged sols was carried out by Billitzer<sup>1</sup> who studied the interaction between ferric oxide and arsenic sulphide sols. He found that the direction of migration of particles under the influence of electro static field is determined by the sol present in excess. Lottermoser<sup>2</sup> while investigating, the mutual coagulation of positive silver iodide sol and negative silver iodide sol, observed that the complete coagulation takes place, when the excess of silver nitrate in one is just equivalent to the excess of potassium iodide in the other. This view point was confirmed by the investigations of Thomson and Johnson.<sup>3</sup> Weiser and Chapman<sup>4</sup> said that this idea of interaction between the stabilising ions can not be true in principle since mutual coagulation was possible in a number of cases, where interaction between the stabilising ions was a remote possibility. According to them, factors responsible for mutual coagulation are (i) mutual adsorption of oppositely charged particles, (ii) the presence of precipitating ions as impurities in the sols, (iii) interaction between stabilising ions.

Hazel and Mc.Queen<sup>5</sup> were of the view that mutual coagulation, is due primarily to mutual adsorption of oppositely charged sol particles, with the consequent unequal redistribution of charges around the particles. Weiser and Milligan<sup>6</sup> observed that the mutual adsorption of sols, lowers the zeta potential of both kinds of particles and that the displacement of counter ions from sols takes place during coagulation. They further observed that during coagulation the  $\text{Cl}^-$  activity of the mixtures increased while that of  $\text{H}^+$  was considerably reduced. They assumed that  $\text{H}^+$  are more strongly adsorbed by ferric oxide while  $\text{Cl}^-$  are weakly adsorbed by copper ferrocyanide.

The present communication is an extention of our work<sup>7</sup> on the variations in the conductivity of copper ferrocyanide sol during coagulation using the hydrous oxide sols of aluminium and chromium as the coagulating agents.

## EXPERIMENTAL

*Copper ferrocyanide Sol* : The method used by Malik and Bhattacharya (*loc. cit.*) was followed to prepare copper ferrocyanide sols (containing increasing amounts of peptising electrolytes). Three samples were thus prepared by mixing 100 ml. of M/50 copper sulphate to 100, 110 and 120 ml. of M/75 potassium ferrocyanide.

*Aluminium Hydroxide Sol* : The method described by Hatschek (Lab. Manual of Colloid Chemistry, 1925, Ed. II, p. 48) was employed for the preparation of this sol. Its strength was determined by coagulating a known vol of the sol by ammonium sulphate and weighing as oxide. The strength was found to be 2.167 gm./litre.

*Chromium Hydroxide Sol* : The method used by Neidle and Barab<sup>s</sup> was followed. Five gms of chromium chloride was dissolved in 20 ml. of doubly distilled water and ammonium hydroxide was added to the boiling solution till the precipitation was complete. The hydrous chromic oxide was allowed to settle, washed thrice by decantation, and finally filtered on a buckner funnel. The precipitate was dissolved in a small portion of boiling 6N hydrochloric continued acid. The solution was evaporated to small bulk filtered and diluted to 750 ml. This resulted in the formation of a sol. It was dialysed for 12 hours with hourly change of water. On dialysis a pinkish coloured sol of conc. 3.14 gms. of Cr<sub>2</sub>O<sub>3</sub>/litre was obtained.

*Zones of mutual coagulation* : Changes in conductance during mutual coagulation were studied under the following conditions. (i) Mixtures of oppositely charged sols. (ii) Mixtures of the oppositely charged sols aged for 15 days.

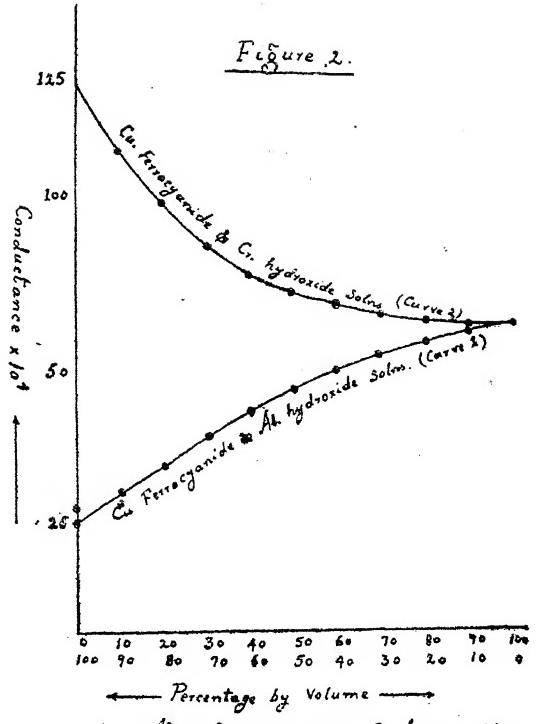
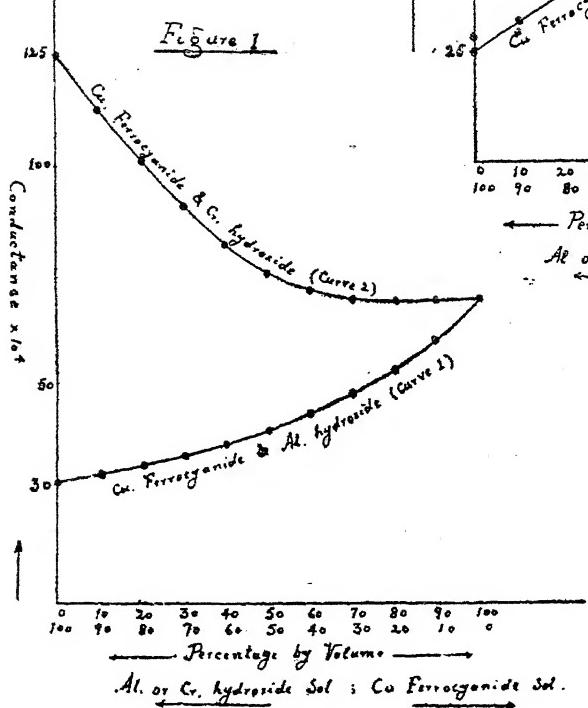
Copper ferrocyanide sol was mixed with Aluminium hydroxide sol, in different proportions and allowed to stand for 24 hours. The region of complete precipitation was found to extend over 20% to 60% of copper ferrocyanide sol. It was rather interesting to find that this region is the same for the three different samples of copper ferrocyanide and was not influenced on varying the amount of peptising electrolyte. The region of complete mutual coagulation for copper ferrocyanide and chromium hydroxide sols determined as above extended from 10% to 90% of copper ferrocyanide sol. In this case also the region of mutual coagulation did not change with the concentration of the peptising electrolyte.

*Conductivity Measurements* : Aluminium hydroxide and copper ferrocyanide sols mixed in different proportions were allowed to stand undisturbed for 24 hours, and the conductivity of the supernatent liquid was measured. The results are represented in Fig. 1 (Curve 1). Experiments were also performed with different copper ferrocyanide sols (containing varying amounts of the peptising electrolyte) and the variation in conductance for different sol mixtures were found to be exactly of the same nature. Similar set of experiments were performed with chromium hydroxide sol. The results are represented graphically in Fig. 1 (Curve 2).

In Fig. 2 results on the variations in conductivity with sols (both +Ve and -Ve) aged for fifteen days are reported. All measurements were carried out at 25  $\pm$  0.1°C.

## DISCUSSION

The variations in conductance suggest that mutual coagulation takes place by the adsorption of oppositely charged sol particles with simultaneous liberation of contra ions. With Al-hydroxide the conductance of the supernatant liquid increases with the proportions of Cu-ferrocyanide sol in the mixture. The fact that the



conductance continues to increase during the zone of complete coagulation is rather interesting. It appears that in the zone of complete coagulation (30 to 60%). The amount of copper ferrocyanide undergoing coalescence continuously increases whilst that of Al-hydroxide is simultaneously decreasing. This results in the liberation of more of  $H^+$  and lesser number of  $Cl^-$ . Since the mobility of  $H^+$  is greater than that of  $Cl^-$ , the conductance continues to increase. The role of adsorption however could not be definitely explained with these results.

The fact that adsorption plays a definite role during mutual coagulation sols is clearly brought out by considering the interaction of chromium hydroxide and copper ferrocyanide sols. As the proportion of copper ferrocyanide sol increases, the conductance of the supernatant liquid falls continuously upto 60% copper ferrocyanide and thereafter it remains constant. The decrease in conductance even after the zone of complete coagulation (10%) clearly indicates the liberation of and subsequent adsorption contra ions. In this case it appears that out of the three antagonistic factors, viz., (i) surface reaction, (ii) liberation of contra ions (iii) adsorption, the latter seems to play a predominant role. The constancy in conductance may be explained by assuming that, with increasing proportion of copper ferrocyanide in the coagulams, the liberation of chloride ions falls and that of hydrogen ion increases; while the adsorbability of the former on the-coagulam falls and that of the latter increases. It is quite probable that after 6% of copper ferrocyanide the two opposing factors balance each other and keep the conductance constant.

#### REFERENCES

1. Billitzer, *Z. Physik. Chem.*, **51**, 129, 1905.
2. Lottemoser, *Kolloid-Z.*, **6**, 78, 1910.
3. Johnson, *J. A. C. S.*, **45**, 2532, 1923.
4. Weiser and Chapman, *J. Phys. Chem.*, **35**, 543, 1931.
5. Hazel and McQueen, *J. Phys. Chem.*, **37**, 553, 1933.
6. Weiser and Milligan, *J. Phys. Chem.*, **47**, 529, 1943.
7. Aijaz & Malik, *J. I. C. S.*, **31**, 755, 1954.
8. Neidle and Barab, *J. A. C. S.*, **38**, 1961, 1916.

**STUDIES ON THE MUTUAL COAGULATION OF SOLS**  
**PART II—CHANGES IN THE H<sup>+</sup> AND CL<sup>-</sup> ACTIVITIES AND ZETA**  
**POTENTIAL DURING THE INTERACTION OF ALUMINIUM AND**  
**CHROMIUM HYDROXIDE SOLS WITH THAT OF COPPER**  
**FERROCYANIDE**

By

MIRZA AIJAZ BEG and WAHID U. MALIK

*Department of Chemistry, Muslim University, Aligarh*

[Received on 24th June, 1959]

**SUMMARY**

Variation in hydrogen and chloride ion as well as the zeta potential have been studied during mutual coagulation. The zeta potentials of the supernatant liquid were determined just after mixing, while the hydrogen and chloride ion activities were measured in the supernatant liquid obtained by keeping the sol mixture over night. The results suggest that coagulation is due to the mutual adsorption of oppositely charged sol particles with the consequent liberation and simultaneous adsorption of contra ions.

Earlier workers like Hardy<sup>1</sup> have shown that stability of a sol is intimately related to the thickness of the double layer, which is directly measured by the zeta potential of the sol. In 1930 Buzagh<sup>2</sup> showed that during electrolytic coagulation, the thickness of the double layer as well as the charge on the particle decreases and this results into a decrease in the zeta potential. The present authors<sup>3</sup> have shown, that during the electrolytic coagulation of copper ferrocyanide sol, the contra ions are continuously liberated and the zeta potential falls with the gradual addition of electrolyte.

In the continuation of our previous work<sup>4</sup> on the mutual coagulation of sols we have employed potentiometric methods to study the mechanism of interaction between copper ferrocyanide and hydrous oxide sols of aluminium and chromium. The studies have been further extended by determining the variation in the zeta potential.

**EXPERIMENTAL**

The three sols, viz., aluminium hydroxide, chromium hydroxide and copper ferrocyanide were prepared by the methods described in the previous communication (*loc. cit.*).

The positive and negative sols were mixed in proportions varying from zero to hundred percent and kept overnight. The concentration of hydrogen ion in the supernatant liquid was determined by means of a potentiometer with a quinhydrone electrode and the other half element being calomel. The results for aluminium and chromium hydroxide sols have been represented in figures 1 and 2 respectively. The pH of the sols after diluting them to the same volume were also measured for comparison sake (figures 1 and 2, Curves 2 and 3).

The chloride ion activity of the supernatant liquids of the above sol mixtures was also measured potentiometrically using Ag-AgCl electrode in conjunction with a standard calomel electrode. The results are represented in figures 1 and 2 (curve 4).

Zeta potential of the sol mixtures was determined by measuring the cataphoretic velocity of the sol particles by Burtons<sup>5</sup> method. For zeta potential measurements ; the sols were mixed in proportions mentioned above and the mixtures were immediately used. With the increasing proportion of copper ferrocyanide sol, the zeta potential decreased continuously till the precipitation stage was reached. And after the zone of complete coagulation, it started to increase again, but the movement of the sol particle was in the other direction. The results are represented below.

TABLE I

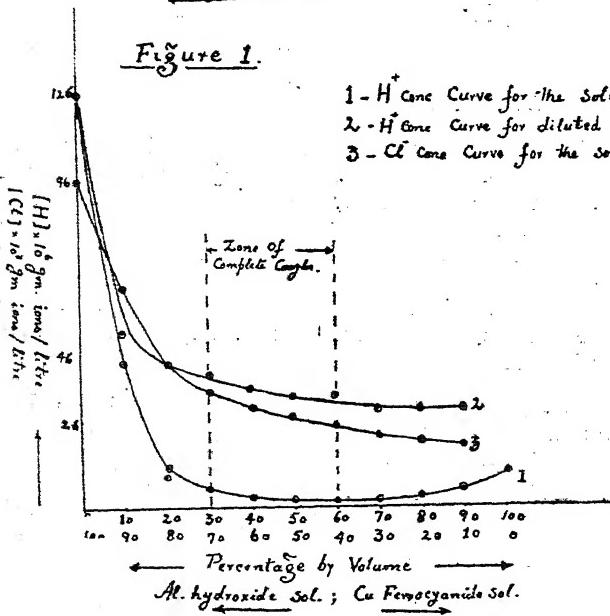
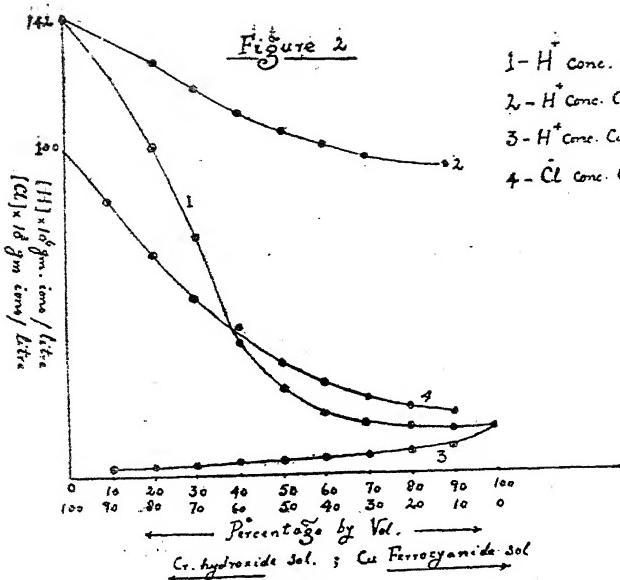
% of Copper ferrocyanide sol.	potential $\times 10^3$ with Al. hydroxide sol	potential $\times 10^3$ with Cr.hydroxide sol.
0	19.7	19.7
10	14.8	14.4
20	9.8	9.6
30	4.95	4.94
40	-	-
50	-	-
60	-	-
70	- 9.8	- 4.94
80	- 14.8	- 9.8

#### DISCUSSION

The results represented in fig. 1 and 2 reveal that as the proportion of copper ferrocyanide sol increased in the sol mixture from zero to 90% the chloride ion actively falls continuously in both the cases ; whereas hydrogen ion activity falls to a minimum (upto 60%) and then rises slowly in the case of aluminium hydroxide while it rapidly falls in the case of chromium hydroxide sol although attaining a constancy in the later stages. Further the hydrogen ion concentration of the sol mixtures in both the cases is lesser than the sum of hydrogen ion concentration of the component sols diluted to the same extent. The later fact clearly indicates that the coagulaum adsorbs hydrogen ions very strongly.

With increasing proportion of copper ferrocyanide in the sol mixture, the hydrogen ion concentration falls continuously in the case of chromium hydroxide and with aluminium hydroxide a slight but regular increase after a minimum is registered. The rapid decrease is due to the increasing proportion of the better adsorbent (copper ferrocyanide particles). In case of aluminium hydroxide sol, the increase in hydrogen ion concentration after the zone of complete coagulation may be due to the decreasing amount of the adsorbent (coagulaum) on partial precipitation.

In both the cases of mutual coagulation described herein, the chloride ion activity falls continuously as the proportion of copper ferrocyanide sol increases in the sol mixture. Since the chloride ion activity of the positive sols is extremely high



whereas that of copper ferrocyanide should be zero, the chloride ion activity should fall with decrease in the proportion of the positive sols and hence would lie between the two extremes. With increasing proportion of the copper ferrocyanide sol, the adsorption of chloride ions should increase resulting in the lowering of chloride ion activity.

On either sides of the zones of complete coagulation there is a region of partial coagulation. Our results on cataphoretic velocity of the supernatant sol reveal that the movement of the sol particles from the two extremes of the zone of complete coagulation is in opposite direction. It suggests that in the earlier sets where the proportion of the negative sol in the sol mixture is very low, the availability of positive to the negative one is very high and that of the negative sol for the positive one is very low. So it is mostly the positive sol particles that are adsorbed on the negative nucleus and comparatively much less is the amount of negative sol that is adsorbed on the positive nucleus; the former adsorption being sufficient enough to lower the zeta potential to the precipitation stage, whilst the latter can only lower the zeta potential. Thus the charge on the partially coagulated sol remains positive and the variation on the other side of the zone of complete coagulation exhibit an altogether reverse behaviour.

#### REFERENCES

1. Hardy, *Z. anorg. allgem. Chem.*, **74**, 174, 1912.
2. Buzagh, *Kolloid. Z.*, **49**, 35, 1929 ; *Naturwiss.*, **8**, 44, 1930.
3. Aijaz and Malik, *J. I. C. S.*, **31**, 759, 1954.
4. Aijaz and Malik, *Proc. Nat. Acad. Sci., India*, **28A**, 316 (1959)
5. Freundlich, Colloid and Capillary Chemistry, p. 262, 1926.

# ON THE EXISTENCE OF HARMONIC SOLUTIONS OF DIFFERENTIAL SYSTEMS

By

V. LAKSHMIKANTHAM and B. VISWANATHAM

*Osmania University, Hyderabad-7 (A. P.)*

[Received on 26th July, 1958]

Consider the Differential System

$$(1) \quad x_i' = f_i(t, x_1, x_2, \dots, x_m) \quad (i = 1, 2, \dots, m)$$

where the functions  $f_i$  are continuous and smooth enough in the domain  $-\infty < t < \infty, -\infty < x_i < \infty$  to ensure the existence and uniqueness of solutions of (1). Let the functions  $f_i$  be periodic in  $t$  with a period unity. The solutions of the system (1) whose period is also unity are called harmonic solutions. Assuming the boundedness of a solution of a system (1) J. L. Massera [2] proved the existence of harmonic solution when  $m = 1$  and  $m = 2$ . He has also given a counter example to the effect that the mere boundness of a solution is not sufficient to ensure the exitence of a harmonic solution when  $m > 2$ . Some sort of additional restriction therefore becomes necessary. The problem is to find out the additional restriction as weak as possible. B. Viswanatham [3] proved the existence of a harmonic solution when  $m > 2$  with the additional condition of monotony on the bounded solution. As observed at the end of the above paper, the monotonic requirement is not quite necessary. The object of this note is to prove the existence of a harmonic solution under less restrictive conditions without assuming the solution to be monotonic.

We require the following results before we proceed further.

*Lemma I.* Let  $E$  be an inductively ordered set and  $T$  be a transformation from  $E$  into  $E$  such that for any  $x$  belonging to  $E$  we have  $T(x) > x$ . Then there is at least one point belonging to  $E$  such that  $T(x) = x$ .

This Lemma is due to Zorn [1].

*Lemma II.* Suppose that (i) the functions  $F_i(t, r_1, \dots, r_m)$  are continuous, bounded and non-decreasing in  $r_i$ , in the domain

$$0 \leq t < \infty, 0 \leq r_i < \infty \quad (i = 1, 2, \dots, m)$$

(ii) The functions  $y_i(t)$  are continuous in  $0 \leq t < \infty$  such that  $y_i(t_1) = c_i > 0$  and satisfy the integral inequality

$$(2) \quad y_i(t) \leq c_i + \int_{t_1}^t F_i(s, y_1(s), \dots, y_m(s)) ds.$$

Then

$$(3) \quad y_i(t) \leq r_i(t) \text{ for } t_1 \leq t < \infty,$$

where  $r_i(t)$  is the unique solution of

$$(4) \quad r_i' = F_i(t, r_1, \dots, r_m)$$

such that  $r_i(t_1) = c_i > 0$ .

**Lemma III.** Suppose that the integral inequality (2) of Lemma II is replaced by

$$(5) \quad y_i(t) \geq c_i + \int_{t_1}^t F_i(s, y_1(s), \dots, y_m(s)) ds.$$

then

$$(6) \quad y_i(t) \geq r_i(t) \text{ for } t^1 \leq t < \infty.$$

The proofs of Lemma II and III follow from the preliminary theorem I in [4], if we assume that the system (4) possesses unique solution.

**Lemma IV.** Let the functions  $F_i$  of the system (4) be non-negative and periodic in  $t$  with a period unity. Suppose that the solution  $r_i(t)$  of (4) through  $(t_1, c_1, \dots, c_m)$  is bounded as  $t \rightarrow \infty$ , then the differential system (4) has a harmonic solution.

**Proof.** Since the function  $F_i$  are assumed to be non-negative, the bounded solution  $r_i(t)$  is monotonic non-decreasing as  $t$  increases. Denote the points  $r_i(t_1) = c_i$  by  $P_0$ . Let the point  $r_i(t_1 + 1)$  be denoted by  $P_1$ . Define the transformation  $T$  which takes any point  $P_0$  into  $P_1$ , obtained by the above process. Thus  $r_i(t_1 + n)$  is the point  $P_n$ . It is clear that all the points  $P_n$  belong to the space  $0 \leq r_i < \infty$ , ( $i = 1, 2, \dots, m$ ). Now the points  $P_n$  form a bounded, monotonic and denumerably infinite set. If their upper bound is included, it becomes an inductively ordered set and Zorn's Lemma 1 shows that there is fixed point  $P$  belonging to the space  $0 \leq r_i < \infty$ . Clearly the components of the fixed point are non-negative. Any solution passing through this fixed point under the above transformations is a harmonic solution since  $F_i$  is periodic in  $t$  with a period unity.

Now we are in a position to prove the following criterion.

**Theorem I.** Let (i) the functions  $h_i(t, r_1, \dots, r_m) \geq 0$  be continuous, bounded, non-decreasing in  $r_i$ , in the domain  $0 \leq t < \infty, 0 \leq r_i < \infty$  and be periodic in  $t$  with a period unity; (ii) the solution of  $r_i(t)$  of the differential system

$$(7) \quad r_i' = h_i(t, r_1, \dots, r_m)$$

passing through  $(t_1, c_1, \dots, c_m)$  be bounded as  $t \rightarrow \infty$ ; (iii) the functions  $f_i(t, x_1, \dots, x_m)$  of the system (1) satisfy the condition

$$(8) \quad |f_i(t, x_1, \dots, x_m)| \leq h_i(|t|, |x_1|, \dots, |x_m|)$$

then the differential system (1) possesses a harmonic solution.

**Proof.** Since the functions  $h_i(t, r_1, r_2, \dots, r_m)$  satisfy the conditions of Lemma IV, it is clear that the differential system (7) possesses a harmonic solution, say,  $H_i(t)$  passing through the fixed point  $P$  such that for a certain  $t = t_0 \geq 0$ ,  $H_i(t_0) = a_i$ . Following the proof of Lemma IV it is clear that  $a_i > 0$ . Now consider the functions  $q_i(t) = H_i(t) - a_i$  which are periodic with a period unity. Now  $q_i(t_0) = 0$  and

$$q_i(t) = \int_{t_0}^t h_i(s, H_1(s), \dots, H_m(s)) ds$$

Since  $h_i$  are non-decreasing and  $q_i(t) \leq H_i(t)$ , we have

$$(9) \quad q_i(t) \geq \int_{t_0}^t h_i(s, q_1(s), \dots, q_m(s)) ds$$

An application of Lemma III yields that

$$(10) \quad q_i(t) \geq y_i(t) \quad \text{for } t_0 \leq t < \infty.$$

where  $y_i(t)$  is a solution of (7) such that  $y_i(t_0) = 0$

Let  $x_i(t)$  be the solution of the differential system (1) such that  $x_i(t_0) = 0$ . Then

$$|x_i(t)| \leq \int_{t_0}^t |f_i(s, x_1(s), \dots, x_m(s))| ds$$

This together with the condition (8) yields

$$|x_i(t)| \leq \int_{t_0}^t h_i(s, |x_1(s)|, \dots, |x_m(s)|) ds.$$

Applying Lemma II we obtain  $|x_i(t)| \leq y_i(t)$  for  $t_0 \leq t < \infty$ .

We obtain from (10)

$$(11) \quad |x_i(t)| \leq y_i(t) \leq q_i(t) \quad \text{for } t_0 \leq t < \infty$$

Now  $x_i(t)$  is the solution of (1) through  $(t_0, 0, \dots, 0)$ . Denote the point  $|x_i(t_0)|$  by  $P_0$ . Take the point  $|x_i(t_0 + 1)|$  on the solution  $x_i(t)$  and denote it by  $P_1$ . Define the transformation  $T$  as one which takes any point  $P_0$  to  $P_1$ , obtained by the above process. Since the functions  $f_i$  are periodic in  $t$  with a period unity, any solution passing through—the fixed point under the above transformation is clearly a harmonic solution. It is therefore enough to, prove the existence of a fixed point under the above transformation. Since  $q_i(t)$  are periodic and  $q_i(t_0) = 0$ , we have  $q_i(t_0 + n) = 0$  for  $n = 0, 1, 2, \dots$ . We therefore obtain from (11) that  $x_i(t_0 + n) = y_i(t_0 + n)$ . But  $y_i(t)$  is non-decreasing as  $t$  increases and hence the points  $|x_i(t + n)|$  form a bounded, monotonic and denumerably infinite set. If their upper bound is included the set becomes inductively ordered. Lemma I shows that we have at least one fixed point. Hence the theorem is proved.

The following theorem is another criterion for the existence of a harmonic solution.

**Theorem II.** Let (i) the functions  $h_i(t, z_1, \dots, z_m) \geq 0$  be continuous, bounded and non-decreasing in  $z_i$ , in the domain  $0 \leq t < \infty, z_i \geq 0$ ;

(ii) the functions  $g_i(t, y_1, \dots, y_m)$  be continuous, bounded and non-decreasing in  $y_i$ , in the domain  $0 \leq t < \infty, y_i \geq 0$ ;

(iii) the functions  $f_i(t, x_1, \dots, x_m)$  of the differential system (1) satisfy the condition

$$(12) \quad g_i(|t|, |x_1|, \dots, |x_m|) \leq f_i(t, x_1, \dots, x_m) \leq h_i(|t|, |x_1|, |x_m|)$$

(iv) the solution  $y_i(t)$  and  $z_i(t)$  of the

differential systems  $z_i = h_i(t, z_1, \dots, z_m)$ ;  $z_i(t_0) = c_i$

$$y_i = g_i(t, y_1, \dots, y_m); y_i(t_0) = c_i$$

respectively be bounded as  $t \rightarrow \infty$  and satisfy

$$y_i(t_0 + n) = z_i(t_0 + n) \quad (n = 0, 1, 2, \dots)$$

then there is a harmonic solution of system (1).

*Proof.* Suppose  $x_i(t)$  is the solution such that  $x_i(t_0) = c_i$ . Then the condition (12) gives

$$x_i(t) \geq c_i + \int_{t_0}^t g_i(s, |x_1(s)|, \dots, |x_m(s)|) ds$$

and

$$x_i(t) \leq c_i + \int_{t_0}^t h_i(s, |x_1(s)|, \dots, |x_m(s)|) ds$$

Applying Lemmas II and III we obtain

$$(13) \quad y_i(t) \leq x_i(t) \leq z_i(t) \quad \text{for } t_0 \leq t < \infty.$$

Since  $y_i(t_0 + n) = z_i(t_0 + n)$  and  $z_i(t)$  is non-decreasing, the points  $x_i(t_0 + n)$  form a bounded, monotonic and denumerably infinite set. If their upper bound is included, the set becomes inductively ordered and hence the result follows.

The existence of a harmonic solution can be proved without using Zorn's Lemma under a different set of conditions as follows :

*Theorem III.* Let (i) the functions  $h_i(t, z_1, \dots, z_m) \geq 0$  be continuous, bounded and non-decreasing in  $z_i$ , in the domain  $0 \leq t < \infty, z_i \geq 0$ ;

(ii) the solution  $z_i(t)$  of the differential system  $z'_i = h_i(t, z_1, \dots, z_m)$ ,  $z_i(t_0) = c_i$  possesses the property  $z_i(t) = 0$  ( $1$ ) as  $t \rightarrow \infty$ ;

(iii) the functions  $f_i(t, x_1, \dots, x_m)$  of (1) satisfy the condition

$$(14) \quad |f_i(t, x_1, \dots, x_m)| \leq h_i(|t|, |x_1|, \dots, |x_m|)$$

(iv) for  $k$  any positive integer, the sequence of functions defined by  $F_i^k(\lambda) = \int^k h_i(\lambda + t, m_1, \dots, m_m) dt$

for fixed values of  $m_i$ , converges uniformly in the interval  $0 \leq \lambda \leq 1$  for each  $i$  ; then there is a harmonic solution.

*Proof.* Let  $x_i(t)$  be the solution of (1) through  $(t_0, c_1, \dots, c_m)$

$$\text{then} \quad |x_i(t)| \leq c_i + \int_{t_0}^t |f_i(s, x_1(s), \dots, x_m(s))| ds$$

$$\text{this gives with (14)} \quad |x_i(t)| \leq c_i + \int_{t_0}^t h_i(s, |x_1(s)|, \dots, |x_m(s)|) ds$$

Applying Lemma II we obtain  $|x_i(t)| \leq z_i(t)$  for  $t_0 \leq t < \infty$ .

But  $z_i(t) = 0$  ( $1$ ) as  $t \rightarrow \infty$ , therefore  $x_i(t)$  is bounded as  $t \rightarrow \infty$ .

This means that

$$(15) \quad |x_i(t)| \leq m_i, \text{ say.}$$

Since the function  $f_i$  are periodic in  $t$  with a period unity, it is enough to consider the values of  $t$  for  $0 \leq t \leq 1$ . Consider the sequence  $A_i^k(t) = x_i(t+k)$  where  $k = 1, 2, \dots$

We shall show that this sequence converges uniformly to  $H_i(t)$ , say. Suppose  $k_1$  and  $k_2$  are any two positive integers such that  $k_2 > k_1$ .

$$\begin{aligned} \text{Then } |A_i^{k_2}(t) - A_i^{k_1}(t)| &= |x_i(t+k_2) - x_i(t+k_1)| \\ &= \left| \int_{t+k_1}^{t+k_2} dx_i(\theta) d\theta/d\theta \right| \\ &= \left| \int_{t+k_1}^{t+k_2} f_i(\theta, x_1(\theta), \dots, x_m(\theta)) d\theta \right| \\ &\leq \int_{t+k_1}^{t+k_2} |f_i(\theta, x_1(\theta), \dots, x_m(\theta))| d\theta. \end{aligned}$$

This together with (14) gives

$$|A_i^{k_2}(t) - A_i^{k_1}(t)| \leq \int_{t+k_1}^{t+k_2} h_i(\theta, |x_1(\theta)|, \dots, |x_m(\theta)|) d\theta$$

Since the functions  $h_i$  are non-decreasing in  $x_i$ , this gives on account of (15)

$$\begin{aligned} |A_i^{k_2}(t) - A_i^{k_1}(t)| &\leq \int_{t+k_1}^{t+k_2} h_i(\theta, m_1, \dots, m_m) d\theta \\ &\leq \int_{k_1}^{k_2} h_i(t+\theta, m_1, \dots, m_m) d\theta \\ &\leq \varepsilon \quad \text{for } k_1, k_2 > k(\varepsilon) \text{ under} \end{aligned}$$

the condition iv of the theorem. Hence  $A_i^k(t)$  converges uniformly to  $H_i(t)$ , say, as  $k \rightarrow \infty$ . Clearly,  $H_i(t)$  satisfies the differential system (1). Again

$$H_i(t+l) = \lim_{k \rightarrow \infty} A_i^{k+l}(t) = \lim_{k \rightarrow \infty} A_i^{k+1}(t) = H_i(t)$$

Hence,  $H_i(t)$  is a harmonic solution of (1). This proves the theorem.

#### REFERENCES

1. Bourbaki : Topologie Générale
2. Massera, J. L. : 'The existence of periodic solutions of systems of differential equations', *Duke Jr. of Maths.* (1950)
3. Viswanatham, B. : 'Existence of harmonic solutions', *Proc. of the Amer. Math. Soc.* (1953)
4. Lakshminarayana, V. : 'Asymptotic problems of non-linear differential systems', *Proc. Nat. Acad. Sci. (India)*, (1958).

# SOIL MOISTURE SYSTEM : WATER CONDUCTION IN SOILS

By

C. L. DHAWAN, P. B. L. BHATNAGAR, TARA SINGH, MANGAL SINGH

*Irrigation & Power Research Institute, Punjab, Amritsar*

[Received on September 3, 1959]

The relation between water and a complex body like soil is one of the most complicated problems in soil physics. These complications enhance in the field due to over changing climatic elements, over which one cannot exercise any control.

It is well known that a soil profile is normally made up of a series of horizons, may be possessing varying physicochemical properties. Therefore, under these conditions, the movement of water is bound to depend directly or indirectly on the properties of the soils, comprising these horizons.

Water is held by the soil in the interstitial space due to surface tension. At saturation, the air-water boundary is plane and the curvature increases as the moisture decreases and hence a greater energy is needed for removing the water from the soil. The curvature of the air water interfaces gradually decreases with the depth. With the decrease in curvature of air water interfaces, the suction pressure also decreases and ultimately it reduces itself to a very negligible quantity that the water it pulls up from the next layer is also very small. A sort of moisture equilibrium is, therefore, set up in a soil profile. This moisture equilibrium is only disturbed by irrigation, rainfall or the change in the climatic elements.

Water is continually being lost from the surface of a bare soil and to a decreasing degree from the lower depths. The upward movement of capillary water takes place against the gravitational potential, when the capillary potential gradient is of sufficient magnitude to produce movement in this direction. Evaporation maintains the upward flow from a water table. McGee (6) observed" that in Great Plains 6 inches of water annually are brought to surface by capillarity from a depth of 10 feet.

Alway and McDole (i) concluded "that the amount of water which the deep sub-soil contributes to the growth of annual plants is of no practical importance". Meteorological observations on moisture changes at the university of Odessa have brought out that 66.2 mm (2) of water in the form of vapour moved from the deeper horizons to the surface during the winter. These results were confirmed by carrying out another experiment at Rostov (2) in 1922-23, when 60 mm of water were calculated to have moved upward from October 7 to March 6. These moisture movement : have been explained on the basis of the differences in vapour pressure created on account of differences in temperature. The recent experiments by Smith (7) indicate that moisture movement in the soil under a temperature gradient can take place by a combination of the forces of capillary potential and vapour movement. The results of Dhawan (5) also point out this phenomenon.

It is an accepted fact that after a small shower of rain or irrigation, a rise in water table takes place, which is considerably greater than can be accounted for by the water applied to the surface.

Dhawan (*loc. cit.*) has given a clear exposition of the moisture relationship, that exists in an unirrigated field having water table at about 15 feet depth by studying the moisture fluctuations for about two years.

From the above discussion, it is clear that the study of the changes in the moisture-status of different soils throws considerable light on their moisture equilibrium relationship on which a judicious programme of irrigation cum agricultural practice can be chalked out. In the light of the above observations, a study was conducted on irrigated, unirrigated, saline and non-saline fields in order to investigate the effect of the change of climatic factors on the moisture equilibrium of these profiles.

#### EXPERIMENTAL

The following six fields were selected for this study :—

- (1) Unirrigated (Fallow) non-saline.
- (2) Unirrigated (Fallow) non-saline.
- (3) Saline field.
- (4) Saline field.
- (5) Field under Berseem (*Trifolium alexandrinum*).
- (6) Field under Berseem (*Trifolium alexandrinum*).

The total soluble salt content and the mechanical analysis of the above fields are given below :—

TABLE I  
Total Salts and Mechanical Analysis of the Profiles

Type of field	Depth in ft.	Total salt %	Clay %	Silt %	Sand %
Normal Fallow Field (A)	0·1	0·20	14·9	19·8	65·3
	1·2	0·19	16·9	23·5	59·6
	2·3	0·20	19·1	23·8	57·1
	3·4	0·17	21·4	25·4	54·2
	4·5	0·15	19·2	26·6	54·3
	5·6	0·11	14·8	30·4	53·2
	6·7	0·10	10·9	25·3	6·88
	7·8	0·09	7·2	26·2	66·6
	8·9	0·09	8·9	15·4	75·7
Normal Fallow Field (D)	0·1	0·11	13·0	35·4	51·6
	1·2	0·07	15·9	25·5	58·6
	2·3	0·06	17·7	25·6	56·7
	3·4	0·08	19·5	24·0	56·5
	4·5	0·09	23·1	20·2	56·7
	5·6	0·07	21·6	20·1	58·3
	6·7	0·12	19·3	19·3	61·4
	7·8	0·07	14·0	15·0	71·0
	8·9	0·08	12·6	15·7	71·7

Type of field	Depth in ft.	Total salt %	Clay %	Silt %	Sand %
Saline Field (A)	0-1	0.50	18.2	16.4	65.4
	1-2	0.55	21.1	23.1	55.8
	2-3	0.47	24.1	24.1	51.7
	3-4	0.39	22.6	23.9	53.5
	4-5	0.26	17.9	33.1	49.0
	5-6	0.14	13.2	27.7	59.1
	6-7	0.15	9.5	13.6	76.9
	7-8	0.12	6.7	8.3	85.0
	8-9	0.10	6.3	8.3	85.4
Saline Field (D)	0-1	0.70	17.8	23.6	58.6
	1-2	0.55	21.6	30.8	47.6
	2-3	0.50	25.5	33.2	41.3
	3-4	0.50	24.7	34.0	41.3
	4-5	0.44	22.4	35.3	42.3
	5-6	0.44	19.2	37.3	43.5
	6-7	0.38	19.3	39.5	41.2
	7-8	0.38	18.5	40.0	41.5
	8-9	0.32	19.1	43.5	37.4
Field under Berseem (C)	0-1	0.09	12.9	21.8	65.3
	1-2	0.13	22.0	26.7	51.3
	2-3	0.10	22.2	27.6	50.2
	3-4	1.10	20.2	30.1	49.7
	4-5	0.10	16.4	34.4	49.2
	5-6	0.12	21.0	42.8	36.2
	6-7	0.10	20.4	40.6	39.0
	7-8	0.10	17.5	39.5	43.0
	8-9	0.10	18.7	28.5	52.8
Field under Berseem (D)	0-1	0.11	13.0	35.4	51.6
	1-2	0.07	15.9	25.5	58.6
	2-3	0.06	17.7	25.6	56.7
	3-4	0.08	19.5	24.0	56.5
	4-5	0.09	23.1	20.2	56.7
	5-6	0.07	21.6	20.1	58.3
	6-7	0.12	19.3	19.3	61.4
	7-8	0.07	14.0	15.0	71.0
	8-9	0.08	12.6	15.7	71.7

The water Table in all the above cases was near about 9.0 ft. depth.

Soil samples were taken at frequent intervals and analysed for moisture content in order to see how far the change in climatic factors was affecting the total moisture equilibrium of the different fields.

#### DISCUSSION OF RESULTS

Table II presents the results of monthly moisture equilibrium of different fields at varying depths.

TABLE II  
Showing the variation in Moisture Equilibrium at Various Depths

Month	Moisture content in inches at various depths							Total
	0—3'	3—6'	6—9'	0—4'	4—8'	8—9'		
<i>Fallow Field (A)</i>								
January	7.59	9.55	11.85	10.49	14.77	4.13	29.39	
February	6.42	9.64	11.89	9.39	14.54	4.12	27.95	
March	5.48	8.89	12.63	8.25	13.81	4.84	27.00	
April	4.57	9.14	11.27	7.47	13.86	3.65	24.89	
May	2.44	8.04	11.18	5.01	12.55	4.10	21.66	
June	2.15	6.94	10.53	3.74	12.17	3.71	19.62	
July	6.38	8.02	12.44	9.59	14.18	4.08	27.85	
Average	5.15	8.66	11.68	7.70	13.70	4.09	25.49	
Standard Deviation	2.0469	0.975	0.686	2.314	0.911	0.359	3.348	
Co-efficient of variation...	<u>39.74</u>	<u>11.25</u>	<u>5.87</u>	<u>29.79</u>	<u>6.65</u>	<u>8.78</u>	<u>13.13</u>	
<i>Fallow Field (D)</i>								
January	7.66	9.04	11.35	10.46	13.41	4.18	28.05	
February	7.00	8.37	10.40	9.75	12.12	3.86	25.73	
March	6.44	7.88	9.66	8.83	11.52	3.63	23.98	
April	4.20	7.22	9.50	6.40	11.27	3.25	20.92	
May	4.08	3.77	8.05	3.86	9.17	2.87	17.90	
June	5.77	4.80	8.30	7.18	8.45	3.24	18.87	
July	10.48	7.64	10.62	12.75	12.07	3.92	28.74	
Average	6.52	7.24	9.70	8.75	11.15	3.56	23.46	
Standard Deviation	2.039	1.4790	1.120	2.276	1.615	0.451	4.188	
Co-efficient of Variation	<u>31.27</u>	<u>20.43</u>	<u>11.55</u>	<u>25.89</u>	<u>14.48</u>	<u>12.66</u>	<u>17.85</u>	
<i>Saline Field (A)</i>								
January	8.29	11.15	13.78	11.71	16.49	5.02	33.22	
February	7.74	11.08	12.53	11.30	15.64	4.41	31.35	
March	7.75	11.16	13.47	11.23	16.90	4.25	32.30	
April	7.78	10.97	12.22	11.29	15.46	4.22	30.97	
May	6.82	10.55	11.67	10.22	14.67	4.15	29.04	
June	6.28	9.69	10.13	9.55	12.29	4.26	26.10	
July	8.97	11.14	12.68	12.54	13.68	4.57	32.49	
Average	7.66	10.82	12.34	11.11	15.30	3.41	30.82	
Standard Deviation	0.8239	0.5023	1.122	0.8395	1.399	0.280	2.347	
Co-efficient of variation...	<u>10.75</u>	<u>4.64</u>	<u>9.09</u>	<u>7.56</u>	<u>9.14</u>	<u>6.37</u>	<u>7.52</u>	

*Berseen Field (D)*

January	...	9.95	13.99	14.58	15.66	19.80	5.06	38.52
February	...	7.63	13.09	15.71	11.62	18.01	4.80	34.43
March	...	...	...	...	...	...	...	...
April	...	8.48	11.50	12.75	11.99	16.26	4.48	32.73
May	...	7.99	11.08	12.44	11.40	15.62	4.49	31.51
June	...	6.25	10.12	11.96	9.45	14.42	4.46	28.33
July	...	7.26	10.14	11.01	10.13	14.47	3.78	28.40
Average	...	7.93	11.65	12.74	11.37	16.43	4.51	32.32
Standard Deviation	...	1.45	1.444	1.58	1.348	1.929	0.362	3.535
Co-efficient of variation	...	14.44	12.40	9.03	11.93	11.74	8.03	10.94

*Saline Field (D)*

January	...	9.21	12.28	13.28	13.14	17.22	4.41	34.77
February	...	8.98	11.85	13.47	12.75	16.89	4.67	34.30
March	...	8.72	12.10	15.52	12.40	17.35	6.59	36.34
April	...	8.31	11.59	13.43	12.01	16.58	4.74	33.33
May	...	6.98	10.48	11.91	10.41	14.98	3.98	29.37
June	...	6.80	9.71	10.78	10.19	13.35	3.85	27.29
July	...	9.41	11.94	12.74	13.35	16.40	4.14	34.09
Average	...	8.34	11.42	13.02	12.05	16.10	4.63	32.78
Standard Deviation	...	0.977	0.886	1.68	1.229	1.339	0.858	2.993
Co-efficient of Variation	...	11.71	75.8	12.66	10.19	8.32	18.55	9.13

*Berseen Field (F)*

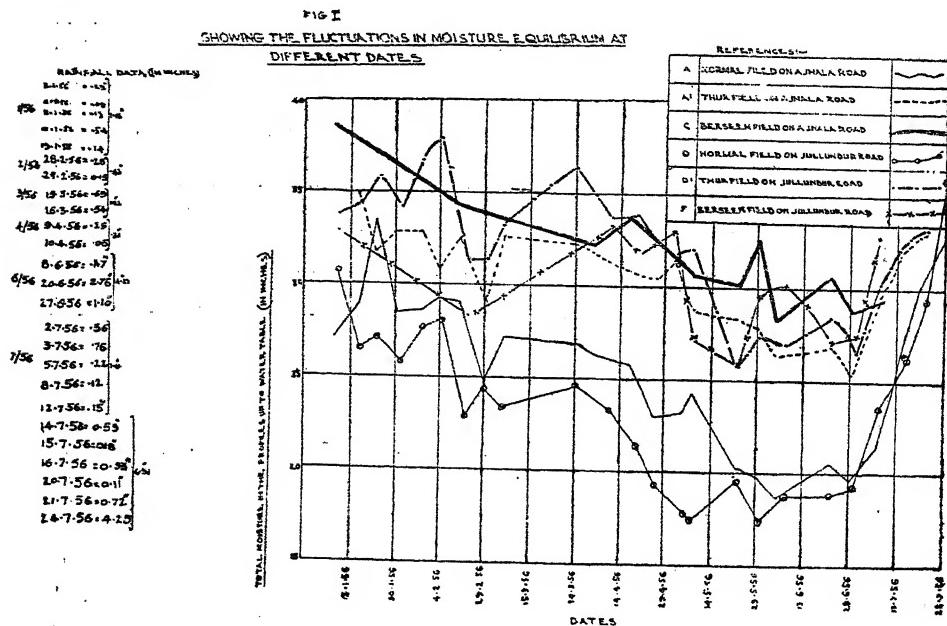
January	...	9.99	10.57	11.45	12.93	14.84	4.19	32.01
February	...	...	...	...	...	...	...	...
March	-	...	...	...	...	...	...	...
April	...	9.61	9.59	13.27	12.72	14.80	4.95	32.47
May	...	8.93	9.27	10.67	11.84	13.42	3.61	28.87
June	...	7.99	9.33	10.69	10.88	13.52	3.63	28.03
July	...	11.39	9.33	12.01	14.64	13.77	4.32	32.73
Average	...	9.58	9.62	11.62	12.61	14.07	4.14	30.82
Standard Deviation	...	1.130	0.486	0.963	1.253	0.623	0.496	1.968
Co-efficient of Variation	...	11.79	5.05	8.31	9.49	4.443	11.98	6.38

Table III shows the comparison of total rainfall with the total moisture in the profile and their average clay content in the profile (percentage of particles below 0.002 mm).

TABLE III

S. No.	Type of Field	Period	Total rainfall in inches	Increase or decrease of total moisture in inches	Average clay % in the whole profile
1.	Normal Fallow (A)	July 14 to July 27	6.34	6.54	14.81
2.	Normal Fallow (D)	July 16 to July 27	5.23	9.30	17.41
3.	Saline A	July 14 to July 27	6.34	5.76	15.52
4.	Saline D	July 16 to July 27	5.23	7.37	20.90

In Fig. I are embodied the fluctuations in total moisture in the different profiles from January to July.



A glance at Table II brings out the following facts.

- (a) The standard deviation and coefficient of variation in the case of fallow fields decrease gradually with depth.
- (b) The standard deviation and coefficient of variation in the case of saline or Berseem fields do not decrease regularly with the depth.

Standard deviation is a measure of the scatter of the observations around their mean. A large standard deviation shows that the frequency distribution is widely spread out from the mean, while a small standard deviation shows that it lies closely concentrated about the mean with little variability between one observation and another.

In order to make a comparison of one standard deviation with another, with widely differing means, the coefficient of variation has been calculated. This coefficient is the standard deviation of the distribution expressed as a percentage of the mean of the distribution.

$$\text{Coefficient of variation} = \frac{\text{Standard deviation}}{\text{Mean}} \times 100.$$

The coefficient of variation gives a better index of the variability of the different observations round their respective means.

It was observed that beyond 3rd to 4th feet depth, there was not much variation in moisture content. This means that in areas where water table is near about 9 feet depth, the climatic factors have got their effect only upto 3rd to 4th feet depth.

During dry months, moisture does leave soil and the loss depends upon the meteorological conditions i. e., temperature, velocity of wind, humidity etc. The total moisture in the profiles went on decreasing until 28th June, when shower of rain increased it. The question arises, "whether we can express the decrease in moisture content in the profiles during the drying period by some simple mathematical expression." Dhawan (4) investigated that all the curves during the different periods of drying were of exponential form and could be represented by the general formula :  $Y=ab^x$ . He determined specific equations for profiles, containing clay content varying from 5 percent to 17 percent. Garbery and Chaklader (3) deduced the following formula :

$$\log (V-H) = k_1 t + k_2$$

The above expression, is imagined by them to be a true measure of the moisture content of the soil at any depth upto the limit of the experiment. V denotes the moisture content, H (the hygroscopic moisture), t the time period and K<sub>1</sub> and K<sub>2</sub> are the constants. K<sub>1</sub> is the coefficient of evaporation. They drew the respective graphs and found out that beyond a particular depth the moisture content remained constant. The cases investigated by Dhawan (4) and Garbery (3) related to uniform type of soil upto water table. But in nature we are not met with a profile having uniform type of soil. Therefore these expressions cannot be applied directly. Due to continuous evaporation during the drying period, there is a gradual loss of moisture upto a certain depth from the top, (3 to 4 feet depth), beyond which there is practically uniform moisture content. The maximum effect is at the end of June, the hottest month of the year.

Table III compares the total rainfall with the total moisture in the profiles. The increase in total moisture is comparatively more in profiles having greater clay content, both in normal and saline soils. This clearly confirms that the finer particles of soil are the greatest governing factors in controlling the moisture equilibrium of a profile. Clays possess a large number of small pores which contribute to a high water-holding capacity. Sands have a greater number of large pores, which are responsible for rapid drainage. From table III, the previous conclusions of Dhawan (5) that rainfall or irrigation flattens the menisci with the reduction in pressure deficiency and therefore a rise in water table is observed, are confirmed. After the rains it was observed that in all the profiles there was a considerable rise in water table as compared with the total rainfall. Secondly, taking into consideration the evaporation and other allied effects, the total increase in moisture in the whole profiles was quite considerable depending upon the average clay content of the profiles. These observations further lend support to the previous conclusions that which the flattening of menisci, there is every possibility of the transfer of that type of water which is held up by the micropores to macropores, which consequently raises the moisture percentage of the soil.

As pointed out in the earlier publication by Dhawan (5), the water which cannot be driven off above  $110^{\circ}\text{C}$  can only be chemically combined water or water held up under such a great tension, that it cannot be released at  $110^{\circ}\text{C}$ . This water may on the flattening of the menisci release some percentage. The greater the clay content, the greater is that type of moisture content held up by the soil, due to the large number of pores (Table III).

#### CONCLUSION

The following points of practical importance are drawn from the above discussion :—

- (i) The total moisture in a profile must be investigated for every foot depth before starting an irrigation for a particular crop, as the amount of irrigation depends upon the type of crop and the total moisture already being held up by the profile.
- (ii) Due to rainfall the increase in total moisture content of the profiles is comparatively more than the total rainfall.
- (iii) The increase in the total moisture content is governed by the average clay content of the profiles. The greater the clay content, the higher is the increase in total moisture content.
- (iv) The standard deviation and coefficient of variation in the case of fallow fields decrease gradually with depth. But the standard deviation and coefficient of variation in the case of saline or berseem fields, do not decrease regularly with the depth.
- (v) The effect of evaporation in profiles, having water table at about nine feet depth is approximately upto 3rd to 4th feet depth.
- (vi) Small irrigations given at frequent intervals are more conducive than large irrigations given at one time.
- (vii) Judicious planning of the water requirement of crops, depending upon the type of crop, total moisture in a profile, and its water table conditions seem very essential before undertaking any irrigation cum agricultural project.

#### REFERENCES

1. Alway, F. J. and McDole, G. R., 1917, "Relation of the water retaining capacity of soil to its hygroscopic coefficient" *J. Agr. Research*, 9:27-71.
2. Baver, L. D., 1948, "Soil physics" P. 245 and 246.
3. Carbery, M and Chakladar, M. N. 1936 "Movement of soil Moisture under field conditions", Indian Journal of Agricultural Science, Vol. VI, P. 1201.
4. Dhawan, C. L., 1954 "Movement of Moisture and salts in soils of Arid Zone" International Commission on Irrigation and Drainage Second Congress B-11, Question 4.
5. Dhawan, C. L., 1954 "Water conduction in unirrigated soils", Annual Bulletin, International Commission on Irrigation and Drainage.
6. McGee, W. J. 1913, "Field records relating to sub soil watter," *U. S. Dept. Agr. Bur. Soils Bull.* 93.
7. Smith W. O. 1944 "Thermal transfer of moisture in soils" *Trans. Am. Geophys. Union.*, 24th Anm. Meeting Hydrol, pp. 511-523.

# ELECTROMETRIC STUDY OF THE INTERACTION BETWEEN ZIRCONIUM NITRATE AND SODIUM ADIPATE AND THE PREPARATION OF ZIRCONIUM ADIPATE GELS

By

R. P. AGARWAL and S. P. MUSHRAN

Chemical Laboratories, University of Allahabad

[Received on 30th December 1959]

## ABSTRACT

Potentiometric and conductometric study of the interaction between zirconium nitrate and sodium adipate has been made. Results at two concentrations of the interacting solutions are recorded. It has been shown that when zirconium : adipate ratio is 1:1 precipitation of the metal mono adipate takes place. The electrometric curves have been explained. Essential conditions of the formation of the metal adipate gels at chosen concentrations of the reactants are described.

In some of the recent publications from these laboratories the preparation of several succinate gels obtained by the metathesis of sodium succinate and metal salt solutions have been described.<sup>1</sup> In other publications the nature of the insoluble succinates separating out as a result of metathesis have been investigated.<sup>2</sup> In this paper the interaction between zirconium nitrate and sodium adipate has been followed by conductometric and potentiometric titration methods. The exact conditions of the formation of the metal adipate gels are also investigated.

## EXPERIMENTAL

**Materials:** Zirconium nitrate employed was of Analar grade. Fresh stock solution of sodium adipate was prepared by neutralising adipic acid (B. D. H.) solution with caustic soda and then making up to the desired concentration.

To a fixed quantity of the zirconium nitrate solution were added different amounts of the sodium adipate solution. The mixtures were shaken for 30 seconds and were then allowed to stand in a circulation bath at  $30 \pm 0.1^\circ$ . The clear solutions gradually gain viscosity and in the course of time set to firm, transparent gels. The gelling time was noted by the method described by Bose and Mushran<sup>3</sup>. The influence of the varying amounts of sodium adipate on the gelling time, for two different concentrations of the interacting solutions may be seen from Tables I and 2.

TABLE I  
Gelling Time depending on the varying amounts of Sodium Adipate.

M Zr (NO <sub>3</sub> ) <sub>4</sub> =4.5 ml. 6	Total Volume=10.0ml.					
M Soda. Adipate 6	... 3.45	3.60	3.75	3.90	4.00 ml	
Gelling time	... 179 (a)	160 (a)	136 (a)	123 (b)	110 mins (b)	
(a) Transparent gel		(b) Gel with slight precipitate				

TABLE 2  
Gelling Time depending on the varying amounts of Sodium Adipate.

M Zr (NO <sub>3</sub> ) <sub>4</sub> =4·50 ml. 12		Total Volume=10·0 ml.				
M Soda. Adipate...		3·50	3·60	3·70	3·80	3·85 ml
12						
Gelling time ...		198	185	174	165	159 mins.
	(a)	(a)	(a)	(b)	(b)	
(a) Transparent gel		(b) Gel with slight precipitate				

#### TITRATIONS

The conductometric titrations were carried out in a thermostat with a bath temperature of  $30 \pm 0\cdot 1^\circ$ . The apparatus consisted of a L & N drum type bridge, length 1000 cm, an audio-oscillator with a tuning fork giving a constant frequency of 1000 C/Sec, a tunable headphone and an immersion cell of the type G. M. 4221.

pH measurements were carried out using a L & N pH meter with a glass electrode at a bath temperature of  $30 \pm 0\cdot 1^\circ$ . The instrument was properly standardised by the determination of its asymmetric potential using a standard solution of potassium hydrogen phthalate.

12 ml. of zirconium nitrate solutions were taken in one set of test tubes and in another set were taken different amounts of sodium adipate. The test tubes were thermostatised at  $30 \pm 0\cdot 1^\circ$ . The reactants were then mixed and several mixtures of the reactants were thus obtained. Each mixture was left undisturbed for an hour and the resistances of such solutions and the pH were recorded. In tables 3 & 4 are recorded the conductivities and the pH for two different concentrations of the interacting solutions.

TABLE 3  
Specific Conductivity and pH depending upon the varying amounts of Sodium Adipate.

M Zr (NO <sub>3</sub> ) <sub>4</sub> =12·0 ml 6		Total Volume=28·0 ml.	
M	Sodium adipate (ml)	pH	Sp. Cond. $\times 10^8 \Omega^{-1}$
0·0		1·60	29·33 )
0·2		1·60	30·30 )
0·5		1·60	30·50 )
0·7		1·62	29·75 ) (a)
2·0		1·68	28·15 )
5·5		1·90	22·78 )
8·0		2·23	19·13 )
9·5		2·77	17·08 )
10·0		3·13	16·53 ) (b)
10·5		3·45	16·73 )
11·0		3·85	17·01 ) (c)
11·5		4·15	17·58 )
13·0		4·65	18·39 )
14·0		4·83	19·16 ) (d)
16·0		5·05	20·53 )

(a) No gel      (b) Transparent gel      (c) Gel with slight precipitate      (d) precipitate

TABLE 4  
Specific Conductivity and pH depending upon the varying amounts of Sodium Adipate.

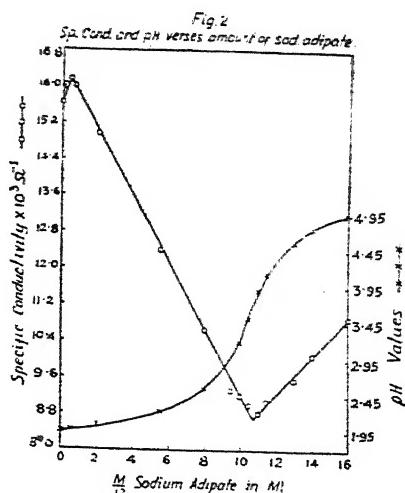
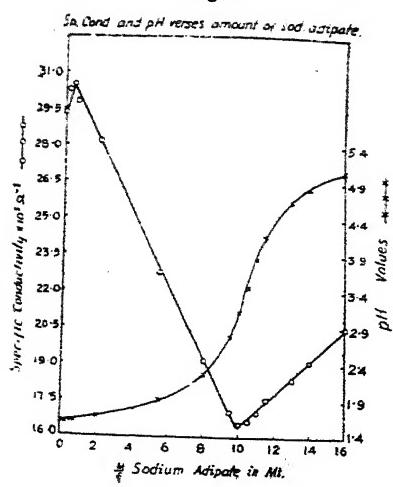
$\frac{M}{12}$  Zr ( $\text{NO}_3$ )<sub>4</sub>=12·0 ml.

Total Volume=28·0 ml.

$\frac{M}{12}$	Sodium adipate (ml)	pH	Sp. Cond. $\times 10^3 \Omega^{-1}$
	0·0	1·95	15·66 )
	0·2	1·95	16·00 )
	0·5	1·98	16·16 )
	0·7	1·98	16·00 ) (a)
	2·0	2·05	14·95 )
	5·5	2·22	12·40 )
	8·0	2·55	10·64 )
	9·5	3·00	9·33 )
	10·0	3·20	9·20 ) (b)
	10·5	3·52	9·00 )
	11·0	3·90	8·81 ) (c)
	11·5	4·10	9·08 )
	13·0	4·55	9·54 )
	14·0	4·75	10·10 ) (d)
	16·0	4·95	10·92 )

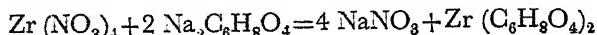
(a) No gel (b) Transparent gel (c) gel with slight precipitate (d) Precipitate

Fig. 1



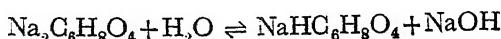
## DISCUSSION

The interaction between a solution of zirconium nitrate and that of sodium adipate may be represented by the simple stoichiometric equation :

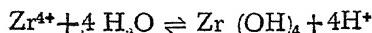


With the addition of larger and larger quantities of sodium adipate solution to a fixed amount of zirconium nitrate, the less conducting  $\text{Zr}^{4+}$  ions will be progressively replaced by the more conducting  $\text{Na}^+$  ions. A gradual increase in the electrical conductance is likely to be observed till the above reaction is complete. and all the zirconium ions are precipitated after which the addition of sodium adipate should bring about a steep rise in electrical conductance. A perusal of Tables 3 and 4 and an inspection of the Figs. 1 and 2 however show that initially there is a slight increase in electrical conductance followed by a drop proceeding upto a minimum after which there is a gradual increase.

A solution of sodium adipate is slightly alkaline due to the reaction—



The low pH (1.60 or 1.95) of zirconium nitrate solution indicates that it is acidic due to the hydrolysis of the salt (*Cf Upadhyaya and Mushran<sup>4</sup>*) as follows:—



The slow initial rise in pH is therefore due to the removal of the hydrogen ions either by formation of water or loss ionised adipic acid.



This suggests a fall in conductance due to the removal of the important contributor in the electrical conductance, namely the hydrogen ions. A distinct rise in conductivity is however perceivable in the early stages. This is easily explained. The removal of the hydrogen ions is also accompanied by the replacement of the  $\text{Zr}^{4+}$  ions by the more conducting  $\text{Na}^+$  ions. The latter effect predominating the former an initial rise in conductivity is observed instead of a decrease.

As more and more of the alkaline adipate is added the decrease in the hydrogen ion concentration becomes more rapid and the conductance consequently falls off rapidly. Figs. 1-2 show that an inflexion in the pH curve occurs when the zirconium, adipate ratio is 1:1. A similar break is indicated in the conductance graph.

On the basis of these results we are led to the conclusion that the precipitate which appears when the adipate, zirconium, ratio is 1:1, is chiefly zirconium mono-adipate, having the formula:— $\text{Zr}(\text{OH})_3(\text{HC}_6\text{H}_8\text{O}_4)$ .

An inspection of Tables 3 and 4 show that the adipate gels prepared with the chosen concentration of the reactants are acidic in nature. We further find from Figs. 1-2 that completion of the reaction takes place a little earlier because the precipitate formed is gelatinous in nature and has a high adsorptive capacity for  $\text{Zr}^{4+}$  ions. It is also seen that a gel results from the interacting solutions in the region where larger proportion of the zirconium mono adipate is present. An essential condition of gel formation is therefore a larger proportion of the metal adipate, which though in the primary stages remains in the colloidal state but in the course of time forms a continuous coherent framework throughout the mass of the solution.

#### ACKNOWLEDGEMENT

Thanks of the authors are due to Prof. S. Ghosh, D.Sc., F.R.I.C., F.N.I. for kind interest during the progress of this work.

#### REFERENCES

1. Bose, S. K. and Mushran, S. P., *Curr. Sci. (India)* **26**, 47 (1957)  
Upadhyaya, Y. D. and Mushran, S. P., *Naturwiss.*, **45**, 514 (1958)
2. Bose, S. K. and Mushran, S. P., *Kolloid-Z.*, **154**, 141 (1957); **158**, 131 (1958)
3. Bose, S. K. and Mushran, S. P., *This Journal*, **27A**, 21 (1958)
4. Upadhyaya, Y. D. and Mushran, S. P., *This Journal*, **28A**, 124 (1959).

# COLORIMETRIC STUDY OF COPPER ION COMPLEX WITH DIHYDROXY BENZOIC ACID (PROTOCATECHUIC ACID)

By

A. SINHA

*Chemical Laboratory, Medical College, Agra*

[ Received on 19th September, 1959 ]

## ABSTRACT

The nature of complexes formed by cupric ions with protocatechuate have been investigated in detail by colorimetric study. It has been observed that in 1 : 1 mixtures of cupric sulphate and mono-potassium protocatechuate, the colour intensifies on increasing pH, and the maximum intensity of colour was noted at pH 5.5. The composition of the complex has been determined at pH 5.5 and 5.2 by Job's method which indicates the formation of a complex containing the reactants in the ratio of 1 : 1 at pH 5.5.

In 1 : 2 and 1 : 3 mixtures of cupric sulphate and monopotassium protocatechuate, the maximum colorimeter readings were noted at pH 5.8, which indicates the formation of another complex other than 1 : 1. The composition of this complex has also been determined by Job's method at pH 5.8 and it contains cupric ion and protocatechuate in 1 : 2 ratio. In between pH 5.5 and 5.8, intermediate mixtures of both the complexes are present.

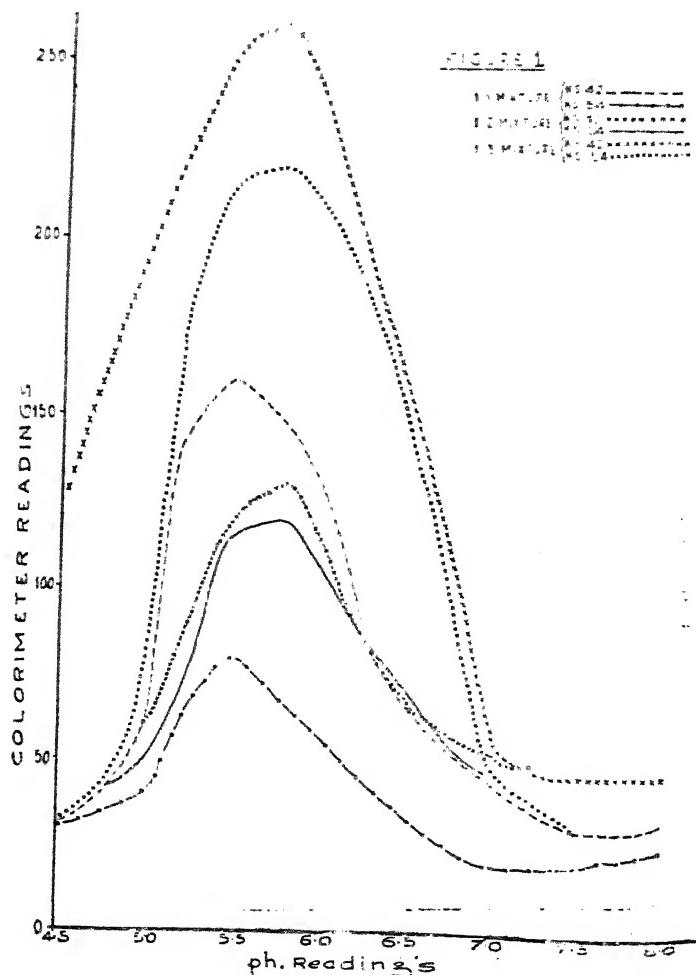
Although studies have been carried out on the complexes formed by cupric ions in aqueous solutions with a variety of organic ligands<sup>1-9</sup>, little systematic physico-chemical work appears to have been carried out on the complexes formed by cupric ions with aromatic hydroxy carboxylic acids and its substituted products. The nature of the complexes present when cupric ions are treated with 3:4 dihydroxy benzoic acid (protocatechuic acid) in aqueous solutions has been investigated by colorimetric measurements carried out with standard molar solutions of cupric sulphate and mono-potassium protocatechuate with potassium hydroxide at different pH.

Standard molar solutions of Analar B. D. H. cupric sulphate and mono-potassium salt of protocatechuic acid obtained by treating B. D. H., L. R. protocatechuic acid with B. D. H. Analar potassium hydroxide was freshly made and used. The readings were taken at a constant temperature of  $27^\circ \pm 0.1^\circ$ , pH measurements were made with an electrically operated Beckman Glass Electrode pH meter and colorimetric readings were taken with a Klett Summerson photo-electric colorimeter using KS 42 and KS 54 filters within the transmission ranges of 400-465 and 500-570 millimicrons respectively.

The method of mono-variation was employed to study the complex formation of copper with mono-potassium protocatechuate and a number of sets of mixtures containing copper sulphate and mono-potassium protocatechuate in the ratios of 1 : 1, 1 : 2 and 1 : 3 were prepared. In order to study Job's method of continuous variation<sup>10</sup>, a constant volume of 50 c. c. of the mixtures of copper sulphate and mono-potassium protocatechuate in varying proportions were prepared at constant pH's 5.5, 5.2, 5.8 and 5.7 respectively.

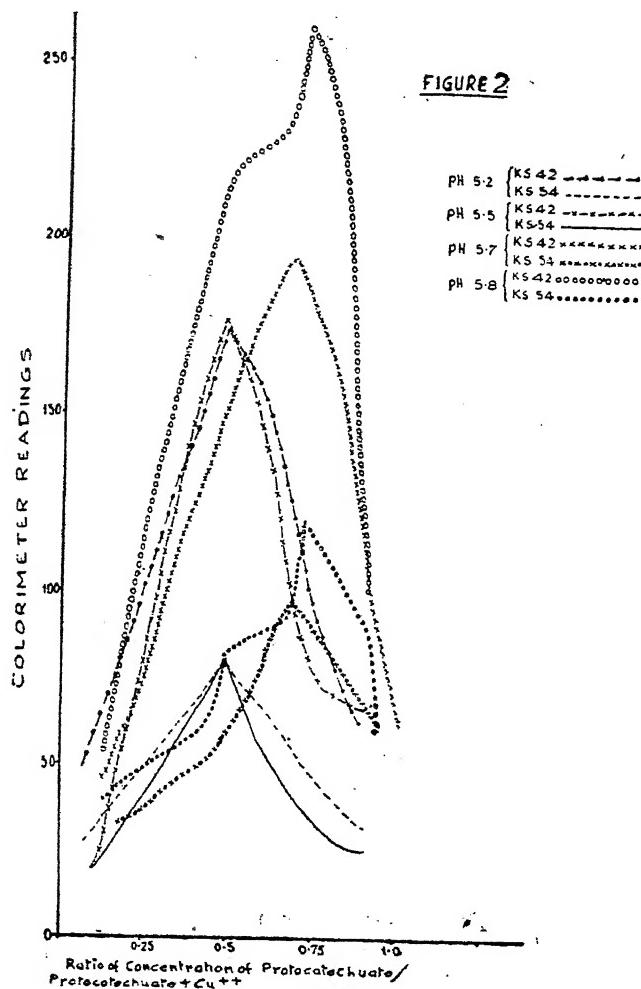
In the graphs, the abscissa represents the pH or the ratio of the concentration of mono-potassium protocatechuate to the total concentration of monopotassium

protocatechuate and cupric ions and the ordinate represents colorimetric readings with the two filters KS 42 and KS 54 respectively. Fig 1 shows the changes in colour with



increase in pH in 1:1, 1:2 and 1:3 mixtures of 0.05 M cupric sulphate and 0.05 M monopotassium protocatechuate. Inference may be drawn that two copper protocatechuate complexes are formed in the system and since the maximum in the colour readings is at pH 5.5 in 1 : 1 mixture and at pH 5.8 in 1 : 2 and 1 : 3 mixtures, it may further be deduced that the formation of two complexes take place at pH 5.5 and at pH 5.8 and above this the complexes break up. The compositions of the copper protocatechuate complexes have been determined by Job's continued variation method<sup>10</sup> using mixtures of 0.05M cupric sulphate and 0.05M mono-potassium protocatechuate in varying ratios from 0.1 to 1.0 of the concentration of mono-potassium protocatechuate and cupric ions taken together at pH 5.2, 5.5, 5.7 and 5.8 while the total volume was kept at 50 c. c.

An examination of the curves in Fig. 2 indicates that the maximum in colorimetric readings were noted at the ratio of 0·5 for mixtures at pH 5·2 and 5·5, 0·65 for mixture at pH 5·7 and at the ratio of 0·7 for the mixture at pH 5·8 which shows



the formation of two complexes, one in 1 : 1 and another in 1 : 2 ratio of cupric sulphate and protocatechuate and also the presence of intermediate mixtures of both the complexes at pH 5·7.

#### ACKNOWLEDGMENT

Thanks of the author are due to Professors M. G. Chakravarti, M.Sc., Ph.D. (London), D.I.C., F.R.I.C. and N. K. Chowdhury, Ph.D. (Edin.), Head of the Departments of Biochemistry and Pharmacology respectively, Medical College, Agra for their keen interest in these investigations.

REFERENCES

1. Babk., *J. Gen. Chem. U. S. S. R.*, **17**, 443 (1947).
2. Yosburgh and Cooper, *J. Amer. Chem. Soc.*, **63**, 437 (1941).
3. Turner and Anderson, *ibid.*, **71**, 912 (1949).
4. Tripathi and Prakash, *J. Indian Chem. Soc.*, **35**, 139 (1958).
5. Mukhedkar and Jatkar, *Symposium on the Chemistry of Co-ordination Compounds (Agra)*, 1959.
6. Mukherji and Dey, *J. Indian Chem. Soc.*, **34**, 461 (1957).
7. Nanda and Pani, *ibid.*, **35**, 355 (1958).
8. Ray, et. al, *ibid.*, **18**, 609 (1941); **21**, 163 (1944).
9. Mukherji and Dey, *Anal. Chim. Acta*, **18**, 324 (1958).
10. Job, et. al, *Ann. Chim.*, **X9**, 113 (1928).

# ROTATORY DISPERSION OF D- AND L-ETHYL AMINO CAMPHOR- $\beta$ -SULPHONATE

By

O. N. PERTI and B. C. PANT

Department of Chemistry, Th. D. S. B. Govt. College, Naini Tal

[Received on 16th December, 1959]

## ABSTRACT

Ethylamine salts of D- and L-camphor- $\beta$ -sulphonic acid have been prepared and characterized. Their rotatory dispersion has been studied in water, methyl alcohol, ethyl alcohol, chloroform and pyridine. In each solvent they exhibit simple dispersion in the visible region. A comparison of their rotatory power with that of ammonium-D-camphor- $\beta$ -sulphonate has been made. It was found that the effect of substitution of electronegative ethyl group in place of electropositive hydrogen is to cause a decrease in the magnitude of rotatory power. The influence of the nature of the solvent and wavelength of light on rotatory power has also been discussed.

## INTRODUCTION

The use of optically active acids for the resolution of racemic bases was introduced by Ladenberg.<sup>1</sup> In 1899 Pope<sup>2</sup> introduced the use of Reychler's<sup>3</sup> D-camphor- $\beta$ -sulphonic acid as a powerful reagent for determining molecular asymmetry and enantiomorphism in organic bases. Schreiber and Shriner<sup>4</sup> have prepared several primary amine salts of Reychler's acid. They found that these salts underwent slight mutarotation in nonaqueous solvents and they ascribed this change to a structural change in which the primary amine salt is converted into a ketimine or anil. However, such a change is not possible in the case of secondary and tertiary amine salts of Reychler's acid. In the present communication the authors have studied ethylamino-(D-and L-) camphor- $\beta$ -sulphonate and compared its rotatory power with that of ammonium-D-camphor- $\beta$ -sulphonate. The influence of chemical constitution, the nature of solvent and wavelength of light on rotatory power has also been discussed.

## EXPERIMENTAL

Reychler's acid was prepared from natural D-camphor essentially according to the method given by Reychler<sup>3</sup> and described earlier by one of us.<sup>5</sup>

L-camphor- $\beta$ -sulphonic acid was prepared from L-camphor obtained by the oxidation of L-isoborneol.

### Ethylamino-camphor- $\beta$ -sulphonate :

6 g. of D- or L- camphor- $\beta$ -sulphonic acid was taken in a dish and neutralized by excess of ethylamine solution. The whole was then evaporated on a water bath. It was then recrystallised from a mixture of ethyl acetate and alcohol. For D-salt - yield 5.6 g.; m. p. 160 - 161°; S = 11.26%. For L-salt - yield 5.4 g.; m. p. 160 - 161°; S = 11.18 %. C10H15OSO3H2N.CH2CH3 requires S = 11.55%.

The salts are white crystalline solid. They are highly soluble in water, methyl alcohol, ethyl alcohol, chloroform and pyridine and practically insoluble in ethyl acetate, carbon tetrachloride, benzene, acetone, ether and petroleum ether.

The rotatory power measurements were carried out in a 2 d cm. tube in different solvents. For the sake of comparison approximately similar concentrations and temperatures were used for each isomer in different solvents. In each case the measurements were carried out for twelve lines in the visible range of the spectrum. The results are recorded in Table 1. It may be mentioned that in twenty four hours no appreciable change in rotatory power was observed.

TABLE I

Rotatory power of ethylamino - camphor -  $\beta$  - sulphonate

Solvent	Water	Methyl alcohol	Ethyl alcohol	Pyridine	Chloroform
Concentration in gm/100 ml	0.9988 1.0028	1.0044 1.0048	1.0048 0.9968	0.9923 1.0000	1.0000 0.9936
$[\alpha]$	$\pm \frac{3.930}{\lambda^2 - 0.12340}$	$\pm \frac{8.177}{\lambda^2 - 0.09888}$	$\pm \frac{8.713}{\lambda^2 - 0.09724}$	$\pm \frac{8.970}{\lambda^2 - 0.09644}$	$\pm \frac{8.976}{\lambda^2 - 0.10150}$
Calculated $\lambda_0$	0.3512	0.3144	0.3118	0.3105	0.3105
Line ( $\lambda$ )	Obs. [ $\alpha$ ] 19.5°				
D -	D -	I -	D -	I -	D -
I -	I -	I -	D -	L -	D -
	+59.07°	-58.83°	-90.14°	+94.04°	+93.80°
Hg <sub>13558</sub>	44.55	44.37	72.68	76.63	76.24
Li <sub>13601</sub>	41.54	41.38	67.70	71.65	71.72
Cd <sub>10778</sub>	36.54	36.89	62.22	62.09	65.63
Cd <sub>4600</sub>	29.03	28.91	51.27	51.08	54.23
Cd <sub>5086</sub>	22.52	22.43	40.82	41.06	43.29
Hg <sub>14161</sub>	18.52	18.44	34.84	34.55	36.82
Hg <sub>6730</sub>	17.52	17.45	32.85	33.05	34.61
Na <sub>55893</sub>	16.01	15.95	29.86	30.04	31.84
Li <sub>16104</sub>	14.01	13.96	26.38	26.54	27.86
Nc <sub>6102</sub>	13.51	13.46	25.88	26.04	27.36
Cd <sub>6439</sub>	12.01	11.96	23.39	23.03	24.38
I <sub>1.6-08</sub>					24.57
					25.18
					25.50
					25.00
					26.60

The values of specific rotations given in Table I were analysed first graphically and then mathematically and the dispersion equations were calculated according to the method given by Lowry.<sup>6</sup> It was found that in each case the rotatory dispersion is simple and can be expressed by Drude's one term equation.

#### DISCUSSION

##### *The Effect of Chemical Constitution on Rotatory Power :*

From the Table 1 it is found that ethylamino-camphor- $\beta$ -sulphonate exhibits "simple" rotatory dispersion as the rotatory power can be expressed by Drude's one term equation,  $[\alpha] = \frac{K}{\lambda^2 - \lambda_0^2}$ , where K is the rotation constant and  $\lambda_0$ , the dispersion constant. In this equation K the rotation constant may be taken as a measure of the rotatory power of the compound where  $\lambda^2 - \lambda_0^2 = 1$  square micron. This hypothetical rotation would correspond to the wavelength in the infra-red region generally beyond 10,000 Å. U. This constant K may be termed the absolute rotation of the compound since it would be independent of the wavelength employed. The authors have previously studied the rotatory power of ammonium-(D- and L-) camphor- $\beta$ -sulphonate in aqueous and non-aqueous solvents.<sup>7</sup> In Table 2 a comparison is made of the optical rotatory power of ammonium and ethylamine salts of Reyhler's acid for Hg<sub>5461</sub>. In this table is also given the values of K within brackets for the sake of comparison.

TABLE 2

*Comparison of Rotatory power of Ammonium<sup>7</sup> and Ethylamino-D-Camphor- $\beta$ -Sulphonates.*

Formula R=C <sub>10</sub> H <sub>15</sub> OSO <sub>3</sub> H	[ $\alpha$ ] <sub>5461</sub> in solvent		
	Water	Methyl alcohol	Ethyl alcohol
R. NH <sub>3</sub>	+27.14° (4.661)*	+ 43.51° (8.280)	+49.00° (9.148)
R. NH <sub>2</sub> .CH <sub>2</sub> .CH <sub>3</sub>	+22.52° (3.930)	+ 40.82° (8.177)	+43.29° (8.713)

From Table 2 it is clear that in water, methyl alcohol and ethyl alcohol ethylamino camphor- $\beta$ -sulphonate exhibits a lower rotation as compared with ammonium-camphor- $\beta$ -sulphonate. This decrease is practically uniform in the whole of the visible region for the twelve wavelengths studied. Similar results are obtained if a comparison is made for the values of K in the three solvents. This result is in accordance with the general rule suggested by Rule<sup>8</sup> and Singh.<sup>9</sup>

##### *The effect of solvent on rotatory power :*

Rule and McLean<sup>10</sup> pointed out that the optically active substances in polar and non-polar solvents exhibit different rotatory power. In the present case it is

\*The values of K are given with in brackets.

found that the magnitude of rotatory power decreases in the order-chloroform > pyridine > ethyl alcohol > methyl alcohol > water, whereas the sequence of increasing dielectric constant is chloroform (5.06) < pyridine (12.42) < ethyl alcohol (25.72) < methyl alcohol (34.7) < water (80). Hence it is observed that the sequence of dielectric constants of the solvents follows the same order as that of rotatory power but in opposite sense. It may be pointed out here that it would be more desirable to compare the dielectric constants of the solutions with optical rotatory power in order to establish the effect of polarity on optical rotatory power.

*The Physical Identity of Enantiomers :*

The magnitudes of optical rotatory power of D- and L- ethylamino camphor- $\beta$ -sulphonates studied in this paper support Pasteur's principle of Molecular Dissymmetry. In 120 observations for twelve wavelengths the differences between D- and L- form is well within experimental error.

ACKNOWLEDGEMENT

We wish to make a grateful acknowledgement to the authorities of Th. D.S.B. Govt. College, Nainital for the provision of research facilities and to Scientific Research Committee, U. P. for the grant of an assistantship to one of us (B. C. P.)

REFERENCES

1. Ladenburg, 1886, *Ber.*, **19**, 2578.
2. Pope, 1899, *J. C. S.*, **75**, 1105.
3. Reyhler, 1898, *Bull. Soc. Chem.*, **19** (iii), 120.
4. Schreiber and Shriner, 1935, *Jour. Amer. Chem. Soc.*, **57**, 1305, 1445, 1896.
5. Perti, O. N., 1954. *Agra. Univ. J. Res. Sci.*, **3**(i), 147.
6. Lowry, 'Optical Rotatory Power', Chap, XXXII.
7. Perti, O. N. and Pant, B. C., 1959, *Agra. Univ. Jour. Res. (Sci.)*, **9**, 1.
8. Rule, 1924, *J. C. S.*, **125**, 1121.
9. Singh, B. K. and Bhaduri, B. N., 1937, *Proc. Ind. Acad. Sci.*, (A.) **6**, 340; 1939, *ibid.*, **IV**, 359 etc.
- Betti, 1923, *Gazz. Chem. et al.*, **53**, 424.
10. Rule and McLean, 1931, *J. C. S.*, 669.

# STUDIES ON THE PRECIPITATION OF THORIUM HYDROXIDE

## PART I. INTERACTION BETWEEN THORIUM CHLORIDE AND AMMONIUM HYDROXIDE

By

RAMESHWAR PRASAD and ARUN K. DEY

*Chemical Laboratories, University of Allahabad, Allahabad*

[Received on 17th December, 1959]

### ABSTRACT

A quantitative study of the association of ions during the precipitation of thorium hydroxide has been made. The precipitation value, i.e., the amount of ammonium hydroxide for the complete precipitation of thorium as thorium hydroxide is nearly equal to the theoretical equivalent. Association of chlorine ions with the precipitate increases upto the addition of 3·8 equivalents of ammonia and finally decreases with excess of ammonium hydroxide added. Adsorption of ammonium ions at first increases and finally decreases with excess of ammonia. The effects of temperature and concentration are not appreciable on the adsorption of ions.

Britton<sup>1</sup> and coworkers in a large number of publications have reported their studies on the precipitation of metal hydroxides, studied mainly by the electrometric method. They observed that for the complete precipitation of the hydroxide, the amount of alkali required is always less than the theoretically equivalent amount. This phenomenon was explained by these authors on the basis of the formation of basic salts of the type  $M(OH)_xAy$  (where M represents the metal and A an anion).

In a number of publications from these laboratories<sup>2</sup> the experimental observations of Britton have been supported. It has been established that an amount of alkali lesser than the equivalent one, completely precipitates the hydrous oxide from its salt solution and thus the precipitated mass has the corresponding anion associated with it. According to Dey and Ghosh<sup>3</sup> the precipitated hydroxide adsorbs the anion on its surface thereby liberating hydroxyl ions which are then responsible for further precipitation of the hydroxide and ultimately leads to complete precipitation.

In this paper, the results of adsorption of ammonium and chlorine ions by thorium hydroxide precipitated from thorium chloride by the progressive addition of ammonium hydroxide have been reported.

### EXPERIMENTAL

**Materials**—A standard solution of thorium chloride (BDH LR) was prepared in carbon dioxide free water and thorium was estimated gravimetrically as thoria. Chlorine ion was also estimated gravimetrically as silver chloride and the ratio of thorium to chlorine was found to be 1:4. A solution of potassium hydroxide was prepared using BDH AnalaR chemical and was standardised against a standard acid using Methyl Red as an indicator. All other chemicals used were of reagent grade.

**Procedure**—In several 100 ml. volumetric flasks, 20 ml. of standard thorium chloride solution were taken, varying amounts of ammonium hydroxide solution were added and the volumes raised to 100 ml. in every case. The precipitates were allowed to settle over night and the supernatant liquids were quantitatively analysed for hydrogen, hydroxyl, chlorine and ammonium ions.

For the estimation of acidity or alkalinity, a known volume was titrated against standard alkali or acid using Methyl Red indicator. Chlorine ion was estimated by titration against standard silver nitrate solution using dichlorofluorescein as an adsorption indicator.

For the determination of ammonium ion, the supernatant liquid was estimated for ammonia by Kjeldahl's method using Pregl's semimicro apparatus. The quantity of ammonia expelled from the liquid was adsorbed in a known amount of sulphuric acid and the unused acid was titrated against standard alkali using a mixed indicator of 1 part of 0·2% Methyl Red and 3 parts of 0·1% Bromocresol Green in alcohol. The adsorption of ammonium ion by the hydroxide was thus calculated knowing the initial amount of ammonium hydroxide added.

All concentrations in the following tables are the final ones and are expressed in mg M or ions per litre.

TABLE I  
Hydrogen Ion Concentration in the Supernatant Liquid after the Precipitation of Thorium Hydroxide.

Concentration of Thorium ions ... = 50 mg ions  
Concentration of Chlorine ions ... = 200 mg ions

Ratio $\text{Th}^{4+} : \text{OH}^-$	Hydrogen Ions in mg ions		
	25°C	50°C	70°C
1 : 3·0	14·0	15·1	15·2
1 : 3·2	10·0	11·6	11·9
1 : 3·4	7·2	9·5	11·0
1 : 3·6	2·7	3·0	3·0
1 : 3·8	0·3	1·1	1·1

TABLE 2  
Hydroxyl Ion Concentration in the Supernatant Liquid after the Precipitation of Thorium Hydroxide

Concentration of Thorium ions ... = 50 mg ions  
Concentration of Chlorine ions ... = 200 mg ions

Ratio $\text{Th}^{4+} : \text{OH}^-$	Hydroxyl Ions in mg ions		
	25°C	50°C	70°C
1 : 4·0	1·0	1·6	1·3
1 : 4·2	1·3	2·4	2·0
1 : 4·4	1·9	2·7	2·5
1 : 4·6	2·5	3·0	3·0
1 : 4·8	2·7	3·1	3·2
1 : 5·0	2·9	4·1	3·8

It is observed that the medium is just alkaline when four equivalents of ammonium hydroxide are added and thorium is completely precipitated with 3·8 equivalents.

TABLE 3  
Adsorption of Ammonium Ions by the Precipitates of Thorium Hydroxide

Concentration of Thorium ions ... = 50 mg ions  
Concentration of Chlorine ions ... = 200 mg ions

Ratio $\text{Th}^{4+} : \text{OH}^-$	Ammonium ions adsorbed in mg ions		
	25°C	50°C	70°C
1 : 3·0	66	80	72
1 : 3·2	67	86	73
1 : 3·4	68	92	74
1 : 3·6	82	100	95
1 : 3·8	64	130	98
1 : 4·0	60	120	107
1 : 4·2	55	100	104
1 : 4·4	49	95	100
1 : 4·6	49	95	95
1 : 4·8	49	95	95
1 : 5·0	48	90	95

From the above table we observe that the adsorption of ammonium ions at 25°C at first increases with the addition of alkali for the precipitation and finally decreases. The same results are observed at the other two temperatures also.

TABLE 4  
Adsorption of chlorine Ions by the Precipitates of Thorium Hydroxide

Concentration of Thorium ions ... = 50 mg ions.  
Concentration of Chlorine ions ... = 200 mg ions

Ratio $\text{Th}^{4+} : \text{OH}^-$	Chlorine ions adsorbed in mg ions		
	25°C	50°C	70°C
1 : 3·0	6·0	26·0	8·0
1 : 3·2	8·0	21·0	10·0
1 : 3·4	10·0	20·0	14·0
1 : 3·6	8·0	16·0	14·0
1 : 3·8	8·0	6·0	14·0
1 : 4·0	6·0	6·5	10·0
1 : 4·2	6·0	5·0	4·0
1 : 4·4	5·0	4·0	2·0
1 : 4·6	4·0	4·0	2·0
1 : 4·8	2·0	1·0	1·0
1 : 5·0	1·0	1·0	1·0

The adsorption of chlorine ions at 25°C, with the addition of ammonium hydroxide for the precipitation, first increases and then finally decreases. At the other temperature *i.e.* at 50°C it decreases. At 70°C the results are similar to that at 25°C.

Experiments were repeated at a lower concentration and the results are given below.

TABLE 5  
Hydrogen Ion Concentration in the supernatant Liquid after the Precipitation of Thorium Hydroxide.

Ratio $\text{Th}^{4+}: \text{OH}^-$	Hydrogen ions in mg ions		
	25°C	50°C	70°C
1 : 3·0	5·1	6·0	8·2
1 : 3·2	4·0	3·5	5·6
1 : 3·4	0·9	1·0	3·2
1 : 3·6	0·1	0·1	2·3
1 : 3·8	0·1	0·1	1·2

TABLE 6  
Hydroxyl Ion Concentration in the supernatant Liquid after the Precipitation of Thorium Hydroxide

Ratio $\text{Th}^{4+}: \text{OH}^-$	Hydroxyl ions in mg ions		
	25°C	50°C	70°C
1 : 4·0	0·2	0·9	1·0
1 : 4·2	2·0	2·5	2·0
1 : 4·4	3·1	3·5	3·1
1 : 4·6	4·5	4·5	4·3
1 : 4·8	5·8	6·0	5·5
1 : 5·0	6·5	6·8	6·5

Here again we observe that the medium becomes alkaline when four equivalents of ammonium hydroxide were added.

TABLE 7

Adsorption of Ammonium Ions by the Precipitates of Thorium Hydroxide

Concentration of Thorium ions	... = 12.5 mg ions
Concentration of Chlorine ions	... = 50.0 mg ions

Ratio Th <sup>4+</sup> : OH <sup>-</sup>	Ammonium Ions adsorbed in mg ions		
	25°C	50°C	70°C
1 : 3.0	22.0	24.0	23.0
1 : 3.2	24.0	26.0	24.0
1 : 3.4	26.0	28.0	26.0
1 : 3.6	27.0	28.0	27.0
1 : 3.8	30.0	30.0	27.0
1 : 4.0	32.0	38.0	28.0
1 : 4.2	28.0	34.0	30.0
1 : 4.4	26.0	31.0	29.0
1 : 4.6	24.0	30.0	25.0
1 : 4.8	23.0	30.0	24.0
1 : 5.0	23.0	28.0	24.0

In the above table we observe the same results as in the Table 3. With the increase of ammonia in the precipitation at 25°C, the adsorption of ammonium ions increases and reaches a maximum at 4 equivalents and then decreases. Similar results are observed at other two temperatures i.e. at 50°C and 70°C.

TABLE 8  
Adsorption of Chlorine Ions by the Precipitates of Thorium Hydroxide

Concentration of Thorium ions	... = 12.5 mg ions
Concentration of Chlorine ions	... = 50.0 mg ions

Ratio Th <sup>4+</sup> : OH <sup>-</sup>	Chlorine Ions adsorbed in mg ions		
	25°C	50°C	70°C
1 : 3.0	2.0	1.0	2.0
1 : 3.2	2.0	2.0	2.0
1 : 3.4	6.0	4.0	6.0
1 : 3.6	8.0	6.0	8.0
1 : 3.8	10.0	8.0	10.0
1 : 4.0	8.0	6.0	8.0
1 : 4.2	7.0	4.5	6.0
1 : 4.4	6.0	4.5	4.0
1 : 4.6	5.5	3.5	4.0
1 : 4.8	2.5	3.0	2.5
1 : 5.0	1.5	2.0	1.5

The results are almost the same as observed in Table 4.

## CONCLUSION

It has been reported earlier<sup>4</sup> that the amount of alkali used for the precipitation of thorium as thorium hydroxide from its salt solution by sodium hydroxide or potassium hydroxide is considerably less than the theoretical amount. From the above tables we may observe that the precipitation values with ammonium hydroxide is very near the theoretical equivalent.

From the quantitative study of the association of chlorine ions with the precipitate, it is interesting to note that the association of chlorine ions at first increases upto the addition of 3·8 equivalents of ammonium hydroxide and then decreases. The association of chlorine ions with the precipitate, in general, diminishes with rise in temperature but remains more or less constant after four equivalents of ammonium hydroxide have been added.

The association of ammonium ion has been recorded in Tables 3 and 7. It may be noted that the association goes on increasing upto four equivalents of ammonium hydroxide but diminishes with excess of the alkali added. The same thing is true when dilute solutions of thorium are employed.

Further work on the behaviour of thorium hydroxide will be described in subsequent communications.

## ACKNOWLEDGEMENTS

The authors express their gratitude to Prof. S. Ghosh and to the late Dr. S. P. Mitra for their interest in the progress of the work. They also thank the Council of Scientific and Industrial Research for supporting the work and for the award of an assistantship to one of them (R. P.).

## REFERENCES

1. Britton, H. T. S., *J. Chem. Soc. (London)* 127, 1899, 2110, 2120, 41 (1925); 129, 269 (1926).  
Britton, H. T. S., and Dodd, E. N., *J. Chem. Soc. (London)* 2464 (1932).  
Britton, H. T. S., and German, Wm., L., *J. Chem. Soc. (London)* 709 (1931).  
Britton, H. T. S., and Young, A. E., *J. Chem. Soc. (London)* 2464 (1932).
2. Ghosh, S., *Presidential Address, Chem. Sect., 45th Ind. Sci. Cong., Madras (1958)*.
3. Dey, A. K., and Ghosh, S., *J. Ind. Chem. Soc.*, **24**, 181 (1947), **27**, 66 (1950).
4. Prasad, R., and Dey, A. K., *Naturwiss. (Communicated)*.

### **EDITORIAL BOARD**

1. Dr. M. S. Randhwa, New Delhi (*Chairman*)
2. Prof. P. S. Gill, Aligarh
3. Prof. K. Banerji, Allahabad
4. Prof. Ram Behari, Delhi
5. Prof. P. L. Srivastava, Allahabad
6. Prof. S. Ghosh, Allahabad
7. Prof. A. K. Bhattacharya, Sagar
8. Prof. N. R. Dhar, Allahabad
9. Prof. S. Ranjan, Allahabad
10. Prof. R. Misra, Varanasi
11. Prof. M. D. L. Srivastava, Allahabad
12. Prof. W. D. West, Sagar
13. Dr. S. P. Raychaudhuri, New Delhi
14. Dr. R. N. Tandon, Allahabad (*Secretary*)

## CONTENTS

<b>Curve of Growth Analysis of <math>\alpha</math> Persei from Neutral Iron Lines . . . . .</b>	<b>R. S. Kushwaha 281</b>
<b>Chemical Examination of the Leaves of the Plant <i>Tinospora Crispa</i> . . . . .</b>	<b>A. Sinha 291</b>
<b>On the Self-Reciprocal Functions for Double Hankel Transforms . . . . .</b>	<b>V. Lakshmikanth 296</b>
<b>Studies on Thiosalts—Part I. . . . .</b>	<b>Keshava Prasad Dubey and Satyeshwar Ghosh 301</b>
<b>Studies on Thiosalts—Part II . . . . .</b>	<b>Keshava Prasad Dubey and Satyeshwar Ghosh 307</b>
<b>A Note on Self-Reciprocal Functions . . . . .</b>	<b>V. Lakshmikanth 312</b>
<b>Studies on the Mutual Coagulation of Sols—Part I . . . . .</b>	<b>Mirza Ajiaz Beg and Wahid U. Malik 316</b>
<b>Studies on the Mutual Coagulation of Sols—Part II . . . . .</b>	<b>Mirza Ajiaz Beg and Wahid U. Malik 320</b>
<b>On the Existence of Harmonic Solutions of Differential Systems . . . . .</b>	<b>V. Lakshmikanth and B. Viswanatham 324</b>
<b>Soil Moisture System : Water Conduction in Soils . . . . .</b>	<b>C. L. Dhawan, B. B. L. Bhatnagar, Tara Singh and Mangal Singh 329</b>
<b>Electrometric Study of the Interaction Between Zirconium Nitrate and Sodium Adipate and the Preparation of Zirconium Adipate Gels . . . . .</b>	<b>R. P. Agarwal and S. P. Mushran 337</b>
<b>Colorimetric Study of Copper Ion Complex with Dihydroxy Benzoic Acid (Protocatechuic Acid) . . . . .</b>	<b>A. Sinha 342</b>
<b>Rotatory Dispersion of D- and L-Ethyl Amino Camphor-<math>\beta</math>-Sulphonate . . . . .</b>	<b>O. N. Perti and B. C. Pant 346</b>
<b>Studies on the Precipitation of Thorium Hydroxide—Part I . . . . .</b>	<b>Rameshwar Prasad and Arun K. Dey 350</b>